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STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION. PART XVII. NITRO- AND CARBOXY- ARYL DERIVATIVES OF STEREOISOMERIC METHYLENECAMPHORS.

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The present communication is a continuation of Parts XII, XV and XVI and describes the optical rotatory dispersion of the condensation products of oxymethylene-camphors (l-, d-, dl-) with nitroanilines (o, m, p-) and aminobenzoic acids (o, m, p-).

p-Nitroanilinomethylenecamphor was prepared according to the method of Pope and Read (*J. Chem. Soc.*, 1909, **95**, 171) and the melting point was found to be identical with that recorded by these authors. This does not agree with that of either of the two forms *viz.* α-form, m.p. 180-81° and β-form, m.p. 151-52° isolated by Rupe and collaborators (*Helv. Chim. Acta*, 1920, **3**, 50). The latter authors do not, however, record any rotatory power data. Pope and Read give the rotation of the dextro compound as $[\alpha]_{Na_D}^{20} = 356\cdot9°$ in benzene; whereas we get $[\alpha]_{Na_D}^{35} = 331\cdot2°$ (Table XV).

m-Nitroanilinomethylenecamphor was also prepared according to the method of Pope and Read (*loc. cit.*) and it melts at 181° instead of 167-68° as recorded by these authors. Our observed value of rotation $[\alpha]_{Na_D} = 249\cdot6°$ in benzene (Table VII) differs from those *viz.* 269·2° (initially) and 233·9° (after 24 hours) given by the above authors. Our compound, however, does not exhibit any mutarotation, a fact which goes against the observation and conclusion of these authors.

o-Carboxyanilinomethylenecamphors (d- and l-), prepared by us, melt at 167-68° and differ from either of the two forms of the same compound *viz.* α-form (m.p. 176°) and β-form (m.p. 112°) isolated by Rupe and collaborators (*loc. cit.*). The authors, however, do not record any rotatory power data,

TABLE A.

$$M = C_8H_{14} \diagdown \begin{matrix} C=CH- \\ | \\ CO \end{matrix} \qquad\qquad [\alpha]^{35°}_{Hg\ green}$$

Compounds.	MeOH.	EtOH.	Acetone.	Pyridine.	CHCl₃.	C₆H₆
*Anilino-M	480·0°	451·3°	448·9°	433·2°	424·6°	367·1°

$$i.e.,\ C_8H_{14} \diagdown \begin{matrix} C=CH\cdot NH- \\ | \\ CO \end{matrix} \diagup\!\!\bigcirc$$

Compounds.	MeOH.	EtOH.	Acetone.	Pyridine.	CHCl₃.	C₆H₆
*m-Toluidino-M	454·4	439·9	442·3	405·8	384·8	352·6
*p-Toluidino-M	465·0	440·8	425·8	401·6	401·6	355·4
†o-Chloroanilino-M	400·2	405·8	380·0	391·3	386·0	364·7
†m-Chloroanilino-M	388·5	384·7	388·0	374·4	381·4	363·6
†p-Chloroanilino-M	417·7	406·3	401·8	394·4	374·6	359·4
‡o-Bromoanilino-M	347·5	339·9	330·1	328·4	329·0	314·3
‡m-Bromoanilino-M	—	354·0	348·4	334·3	324·1	279·3
‡p-Bromoanilino-M	361·1	355·6	360·6	348·8	324·3	291·9
‡m-Iodoanilino-M	328·5	319·5	309·7	294·8	279·1	251·1
‡p-Iodoanilino-M	338·1	325·9	326·5	318·4	300·0	258·6
o-Nitroanilino-M	**493·1	—	**468·1	**424·8	**484·6	399·2
m-Nitroanilino-M	393·9	—	389·2	367·1	350·0	315·6
p-Nitroanilino-M	510·7	—	519·4	545·0	493·5	437·0
o-Carboxyphenylamino-M	388·9	388·5	373·5	377·5	382·2	395·6
m-Carboxyphenylamino-M	396·8	390·9	376·1	371·5	—	—
p-Carboxyphenylamino-M	—	—	—	426·3	—	—

* Singh, Bhaduri and Barat, *J. Indian Chem. Soc.*, 1931, **8**, 345.
† Singh and Bhaduri, *Proc. Indian Acad. Sci.*, 1937, **6A**, 340
‡ Singh and Bhaduri, *ibid.*, 1939, **10A**, 359
** Extrapolated values from the equations.

Effect of Chemical Constitution on the Rotatory Power.—Since polar effect of a substituent group is traceable in optical activity (Singh and Bhaduri, Parts XV and XVI; Betti, *Gazzetta*, 1923, **53**, 424) we

should expect that the substitution of positive groups such as $-NO_2$ and COOH in anilinomethylenecamphors will increase the rotation of the parent compound, and the effect would be most marked in the case of *ortho*-substituents owing to the close proximity of the substituent group. The nitro substituent in the *ortho* and *para* positions has the maximum rotation amongst the series of substituent groups so far examined (*cf.* Table A) and the rotation in the *meta* position is intermediate. The position of COOH group is anomalous; in the sequence of substituent groups, as a positive group, it ought to be in the proximity of NO_2, another strongly positive one. But it is always intermediate in the series, with no fixed position. Except in benzene in the case of *ortho*-substituents, nowhere is the polar sequence strictly followed; the position of COOH-group being most uncertain of the series. A similar irregularity is observed in the position of the COOH-group amongst the different groups of the "molecular inductive capacity" series (Rule and Smith, *J. Chem. Soc.*, 1925, 2188).

Nature of the Solvent and Rotatory Power.—There is no regular sequence of the solvents; although in previous communications it was observed that the sequence of the solvents with reference to optical rotation was more or less similar to that of their dielectric constants.

Position Isomerides and Rotatory Power.—The sequence of the rotatory power of the position isomerides of nitroanilinomethylene-camphors is in general $p > o > un > m$ in all the solvents. This is neither in agreement with Frankland's lever arm hypothesis (*J. Chem. Soc.*, 1896, **69**, 1583) nor with the electrostatic modifications suggested by Rule (*J. Chem. Soc.*, 1924, **125**, 1122) as according to either of the two, *meta* should be always intermediate between *ortho* and *para*. A similar line of discussion may be extended to the position isomerides of carboxyanilinomethylenecamphors for which the order in pyridine is $un > p > o > m$.

Physical Identity of Isomers.—The values of rotatory power of *d*- and *l*- forms in different solvents (Table I-XXVI) are identical within the limits of experimental error. Out of 195 observations now recorded, in as many as 152 cases difference in the numerical value of the specific rotatory power of the opposite isomers corresponds to a difference of less than $0.01°$ in the observed angle of rotation and in 36 cases the corresponding angle lies between $0.01°$ and $0.02°$, which is the limit of experimental error allowable in such measurements. Only in 7 cases, the difference corresponds to between $0.02°$ and $0.03°$ in the observed angle of rotation. All these are, however, of the nature of casual

experimental errors. This, therefore, further supports Pasteur's principle of molecular dissymmetry according to which the two forms, d- and l- must possess equal and opposite rotatory power.

The melting points of the racemic forms of p-nitroanilinomethylene-camphor and p-carboxyphenylaminomethylenecamphor are higher than those of the optically active forms. These forms are dl-compounds at least in the solid state.

The Nature of Rotatory Dispersion.—The compounds described in this paper obey the simple dispersion law, $[\alpha] = \dfrac{k}{\lambda^2 - \lambda^2_0}$. In the numerical test given in the tables of rotatory dispersion [I-XXVI], this point is clearly brought out as the differences in the observed and calculated values of rotatory power lie well within the limits of experimental error.

<center>E X P E R I M E N T A L.</center>

The *laevo* and the *racemic* compounds described in the present paper were prepared in the same way as the corresponding *dextro* isomers and had the same crystalline form and similar solubility.

General Method of Preparation.—Oxymethylenecamphor (1 mol.), dissolved in methyl alcohol, was added to the solution of the base (1 mol.) in glacial acetic acid when a precipitate separated at once or on keeping and vigorous scratching. It was then crystallised from a suitable solvent.

o-*Nitroanilinomethylene*-d-*camphor*, m.p. 157-58°, was obtained as orange-red needles, easily soluble in chloroform and acetone, less so in pyridine and sparingly soluble in ether, ethyl and methyl alcohol and benzene. (Found: C, 67·98; H, 6·87. $C_{17}H_{20}O_3N_2$ requires C, 67·94; H, 6·71 per cent).

o-*Nitroanilinomethylene*-l-*camphor* melts at 158°. (Found: N, 9·40. $C_{17}H_{20}O_3N_2$ requires N, 9·33 per cent). o-*Nitroanilinomethylene*-dl-*camphor* melts at 150°. (Found: N, 9·49%).

m-*Nitroanilinomethylene*-d-*camphor*, m.p. 181°, was obtained as bright yellow small crystals. (Found: C, ·67·81; H, 6·99. $C_{17}H_{20}O_3N_2$ requires C, 67·94; H, 6·71 per cent). It is easily soluble in chloroform and acetone, less so in pyridine and sparingly soluble in ether, methyl alcohol, ethyl alcohol and benzene. m-*Nitroanilinomethylene*-l-*camphor*

melts at 180-81°. (Found : N, 9·64. $C_{17}H_{20}O_3N_2$ requires N, 9·33 per cent). m-*Nitroanilinomethylene*-dl-*camphor* melts at 167-68°. (Found: N, 9·48%).

p-*Nitroanilinomethylene*-d-*camphor*, m.p. 154-55°, was obtained as bright yellow shining needles. (Found : C, 67·96 ; H, 7·05. $C_{17}H_{20}O_3N_2$ requires C, 67·94 ; H, 6·71 per cent). It is easily soluble in chloroform and acetone, less so in pyridine and sparingly soluble in ether, methyl alcohol, ethyl alcohol and benzene.

p-*Nitroanilinomethylene*-l-*camphor* melts at 154-55°. (Found : N, 9·47. $C_{17}H_{20}O_3N_2$ requires N, 9·33 per cent). p-*Nitroanilinomethylene*-dl-*camphor* melts at 167-68°. (Found : N, 9·48%).

o-*Carboxyphenylaminomethylene*-d-*camphor*, m.p. 166-67°, was obtained as pale yellow rectangular plates. (Found : C, 72·01 ; H, 7·38 ; N, 4·78. $C_{18}H_{21}O_3N$ requires C, 72·24 ; H, 7·02 ; N, 4·68 per cent). It is easily soluble in chloroform, pyridine, acetone and ether, less so in benzene, ethyl alcohol and methyl alcohol. o-*Carboxyphenylaminomethylene*-l-*camphor* melts at 167-68°. (Found : N, 4·72. $C_{18}H_{21}O_3N$ requires N, 4·68 per cent). o-*Carboxyphenylaminomethylene*-dl-*camphor* melts at 113°. (Found : N, 4·70%).

m-*Carboxyphenylaminomethylene*-d-*camphor*, m.p. 219-21°, was obtained as colourless needles. (Found : C, 72·02 ; H, 7·26. $C_{18}H_{21}O_3N$ requires C, 72·24 ; H, 7·02 per cent). It is fairly soluble in pyridine, less so in methyl alcohol and ethyl alcohol and sparingly soluble in ether, benzene and chloroform. m-*Carboxyphenylaminomethylene*-l-*camphor* melts at 219-21°. (Found : N, 4·70. $C_{18}H_{21}O_3N$ requires N, 4·68 per cent). m-*Carboxyphenylaminomethylene*-dl-*camphor* melts at 215-17°. (Found : N, 4·88%).

p-*Carboxyphenylaminomethylene*-d-*camphor*, m.p. 280-83°, was obtained as long rectangular plates. (Found : C, 72·09 ; H, 7·27. $C_{18}H_{21}O_3N$ requires C, 72·24; H, 7·02 per cent). It is moderately soluble in pyridine and sparingly soluble in ordinary organic solvents. p-*Carboxyphenylaminomethylene*-l-*camphor* melts at 280-82°. (Found : N, 4·70%). p-*Carboxyphenylaminomethylene*-dl-*camphor*, m.p. 283-85°, was obtained as needles. (Found : N, 4·73%).

The rotatory power determinations were made in a 2-dcm. jacketed tube at 35°. The value of λ_0, calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm.

TABLE I.

o-*Nitroanilinomethylenecamphor in chloroform.*

$$[\alpha] = \pm \frac{45.54}{\lambda^2 - 0.2042} \; ; \; \lambda_0 = 0.4519.$$

	Dextro.					Laevo.	
Conc. (g./100 c.c.)	Obs [α]. o.	o−c.	Line.	Calc. [α]. c.	o'−c.	Obs.[α]. o'.	Conc. (g./100 c.c.)
0.4036	+350.6°	+1.5°	Hg5780	±349.1°	+0.8°	−349.9°	0.4016
,,	315.9	−1.5	Na5893	317.4	−1.2	316.2	,,
,,	270.1	+0.7	Li6104	269.4	+0.8	270.2	,,
,,	216.6	+0.6	Cd6438	216.0	+0.6	216.6	,,
,,	185.8	+0.9	Li6708	184.9	+0.6	185.5	,,

TABLE II.

o-*Nitroanilinomethylenecamphor in benzene.*

$$[\alpha] = \pm \frac{50.26}{\lambda^2 - 0.1729} \; ; \; \lambda_0 = 0.4158.$$

	Dextro					Laevo.	
Conc. g./100 (c.c.)	Obs.[α]. o.	o−c.	Line.	Calc.[α]. c.	o'−c.	Obs [α]. o'.	Conc. (g./100 c.c.)
0.4020	+399.2°	−2.0°	Hg5461	±401.2°	−1.0°	−400.2°	0.4008
,,	314.2	+2.4	Hg5780	311.8	+1.2	313.0	,,
,,	288.5	±0	Na5893	288.5	−0.5	288.0	,,
,,	250.0	−1.2	Li6104	251.2	+0.7	251.9	,,
,,	206.4	−1.6	Cd6438	208.0	−1.0	207.0	,,
,,	180.1	−1.4	Li6708	181.5	+0.5	182.0	,,

TABLE III.

o-*Nitroanilinomethylenecamphor in methyl alcohol.*

$$[\alpha] = \pm \frac{57.80}{\lambda^2 - 0.1810} \; ; \; \lambda_0 = 0.4254.$$

	Dextro.					Laevo.	
Conc. (g./100 c.c.)	Obs.[α]. o.	o−c.	Line	Calc.[α]. c.	o−c.	Obs.[α]. o'.	Conc (g./100 c.c.)
0.4012	+378.9°	+2.9°	Hg5780	±376.0°	+1.5°	−377.5°	0.4016
,,	349.0	+1.6	Na5893	347.4	+0.6	348.0	,,
,,	300.4	−2.1	Li6104	302.5	−0.8	301.7	,,
,,	248.0	+0.2	Cd6438	247.8	−0.3	247.5	,,
,,	215.6	+0.7	Li6708	214.9	±0	214.9	,,

TABLE IV.

o-Nitroanilinomethylenecamphor in acetone.

$$[\alpha] = \pm \frac{59 \cdot 07}{\lambda^2 - 0 \cdot 1720}; \; \lambda_0 = 0 \cdot 4147.$$

	Dextro.						Laevo.	
Conc.	Obs.[α].	o−c.	Line.	Calc.[α].	o′−c.	Obs.[α].	Conc.
(g./100 c.c.)	o.			c.		o′.	(g./100 c.c.)
0·4020	+364·4°	±0°	Hg$_{5780}$	±364·4°	−0·6°	−363·8°	0·4000
,,	337·0	−0·5	Na$_{5893}$	337·5	−1·3	336·2	,,
,,	294·7	+0·2	Li$_{6104}$	294·5	+0·5	295·0	,,
,,	243·8	+0·2	Cd$_{6438}$	243·6	+0·1	243·7	,,
,,	212·5	±0	Li$_{6708}$	212·5	−1·2	211·3	,,

TABLE V.

o-Nitroanilinomethylenecamphor in pyridine.

$$[\alpha] = \pm \frac{72 \cdot 06}{\lambda^2 - 0 \cdot 1286}; \; \lambda_0 = 0 \cdot 3586.$$

	Dextro.						Laevo.	
Conc.	Obs.[α].	o−c.	Line.	Calc.[α].	o′−c.	Obs.[α].	Conc.
(g./100 c.c.)	o.			c.		o′.	(g./100 c.c.)
0·4000	+350·0°	−0·5°	Hg$_{5780}$	±350·5°	+1·2°	−351·7°	0·4024
,,	330·0	+0·2	Na$_{5893}$	329·8	−0·5	329·3	,,
,,	296·2	+0·9	Li$_{6104}$	295·3	+0·4	295·7	,,
,,	251·3	−0·8	Cd$_{6438}$	252·1	+1·3	253·4	,,
,,	223·8	−0·5	Li$_{6708}$	224·3	−0·6	223·7	,,

Table VI.

m-*Nitroanilinomethylenecamphor in chloroform.*

$$[\alpha] = \pm \frac{68\cdot 63}{\lambda^2 - 0\cdot 1022} \; ; \; \lambda_0 = 0\cdot 3196$$

Dextro.						Laevo.		
Conc. (g./100 c.c.)	Obs.[α]. o.	o−c.	Line.	Calc.[α]. c.	o′−c.	Obs.[α]. o′.	Conc. (g./100 c.c.)
0·4028	+405·7°	−0·1°	Ag$_{5209}$	±405·8°	−0·5°	−405·3°	0·4036
,,	350·0	−0·1	Hg$_{5461}$	350·1	+0·4	350·5	,,
,.	296·7	+0·8	Hg$_{5780}$	295·9	+0·2	296·1	,,
,.	280·5	+0·3	Na$_{5893}$	280·2	−0·2	280·0	.,
.,	254·5	+0·7	Li$_{6104}$	253·8	+0·2	254·0	,,
,.	219·8	±0	Cd$_{6438}$	219·8	−0·5	219·3	,,
,.	197·3	±0	Li$_{6708}$	197·3	+0·9	198·2	,,

Table VII.

m-*Nitroanilinomethylenecamphor in benzene.*

$$[\alpha] = \pm \frac{57\cdot 73}{\lambda^2 - 0\cdot 1152} \; ; \; \lambda_0 = 0\cdot 3394.$$

Dextro.						Laevo.		
Conc. (g./100 c.c.)	Obs. [α] o.	o−c.	Line.	Calc. [α]. c.	o′−c.	Obs. [α] o′.	Conc. (g./100 c.c.)
0·4008	+401·8	−0·6°	Cd$_{5086}$	±402·4°	+1·3°	−403·7°	0·4012
,,	370·6	+0·4	Ag$_{5209}$	370·2	−0·1	370·1	,,
,,	315·6	−0·2	Hg$_{5461}$	315·8	+0·7	316·5	,,
,,	314·5	+0·3	Ag$_{5463}$	314·2	—	—	,,
,,	263·2	−0·5	Hg$_{5780}$	263·7	−0·8	262·9	,,
,,	249·6	+0·6	Na$_{5893}$	249·0	−1·0	248·0	,,
,,	224·6	+0·3	Li$_{6104}$	224·3	+0·1	224·4	,,
,,	193·4	+0·5	Cd$_{6438}$	192·9	+0·3	193·2	,,
,,	172·2	−0·3	Li$_{6708}$	172·5	−0·5	172·0	

TABLE VIII.

m-Nitroanilinomethylenecamphor in methyl alcohol.

$$[\alpha] = \pm \frac{79 \cdot 36}{\lambda^2 - 0 \cdot 0974}; \quad \lambda_0 = 0 \cdot 3121.$$

Dextro.						Laevo.		
Conc. (g./100 c.c.).	Obs. [α]. o.	o−c.	Line.	Calc. [α]. c.	o″−c.	Obs. [α]. o′.	Conc. (g./100 c.c.)
0·4012	+457·4°	+1·7°	Ag$_{5209}$	±455·7°	±0°	−455·7°	0·4024
,,	393·9	−1·4	Hg$_{5461}$	395·3	−0·2	395·1	,,
,,	333·9	−1·4	Hg$_{5780}$	335·3	+0·2	335·5	,,
,,	316·5	−1·3	Na$_{5893}$	317·8	+0·3	318·1	,,
,,	289·2	+0·8	Li$_{6104}$	288·4	−0·2	288·2	,,
,,	249·2	−1·0	Cd$_{6438}$	250·2	−0·4	249·8	,,
,,	225·1	±0	Li$_{6708}$	225·1	+1·0	226·1	,,

TABLE IX.

m-Nitroanilinomethylenecamphor in pyridine.

$$[\alpha] = \pm \frac{69 \cdot 80}{\lambda^2 - 0 \cdot 1080}; \quad \lambda_0 = 0 \cdot 3295.$$

Dextro.						Laevo.		
Conc. (g./100 c c.)	Obs. [α]. o.	o−c.	Line.	Calc. [α]. c.	o′−c.	Obs. [α]. o′.	Conc. (g./100 c.c.)
0·4004	+367·1°	−0·1°	Hg$_{5461}$	±367·2°	−0·5°	−366·7°	0·4008
,,	365·9	+0·4	Ag$_{5468}$	365·5	+0·1	365·6	,,
,,	309·7	+1·0	Hg$_{5780}$	308·7	−0·5	308·2	,,
,,	291·0	−1·0	Na$_{5893}$	292·0	−0·3	291·7	,,
,,	264·7	+0·7	Li$_{6104}$	264·0	+0·4	264·4	,,
,,	228·6	+0·8	Cd$_{6438}$	227·8	+0·5	228·3	,,
,,	204·5	+0·3	Li$_{6708}$	204·2	+0·4	204·6	,,

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TABLE X.

m-Nitroanilinomethylenecamphor in acetone.

$$[\alpha]= \pm \frac{69\cdot47}{\lambda^2-0\cdot1204}; \ \lambda_0=0\cdot3470.$$

Dextro.						Laevo.	
Conc. (g./100 c.c.)	Obs. [α]. o.	o−c.	Line.	Calc. [α]. c.	o′−c.	Obs [α]. o′.	Conc. (g./100 c.c.)
0·4020	+461·3°	+0·8°	Ag₅₂₀₉	±460·5°	+0·2°	−460·7°	0·4024
,,	389·2	−1·4	Hg₅₄₆₁	390·6	+0·3	390·9	,,
,,	388·1	−0·9	Ag₅₄₆₈	389·0	—	—	,,
,,	323·3	−1·8	Hg₅₇₈₀	325·1	−0·2	324·9	,,
,,	307·2	+0·8	Na₅₈₉₃	306·4	−0·1	306·3	,,
,,	274·9	−0·6	Li₆₁₀₄	275·5	+1·0	276·5	,,
,,	236·3	+0·1	Cd₆₄₃₈	236·2	+0·4	236·6	,,
,,	211·3	+0·5	Li₆₇₀₈	210·8	−0·4	210·4	,,

TABLE XI.

p-Nitroanilinomethylenecamphor in chloroform.

$$[\alpha]= \pm \frac{74\cdot49}{\lambda^2-0\cdot1476}; \ \lambda_0=0\cdot3842.$$

Dextro.						Laevo.	
Conc. (g./100 c.c.)	Obs. [α]. o.	o−c.	Line.	Calc. [α]. c.	o′−c.	Obs. [α] o′.	Conc. (g./100 c.c.)
0·4008	+670·1°	−0·4°	Cd₅₀₈₅	±670·5°	−1·4°	−669·1°	0·4020
,,	601·3	−0·9	Ag₅₂₀₉	602·2	−0·3	601·9	,,
,,	493·5	−1·1	Hg₅₄₆₁	494·6	+0·4	495·0	,,
,,	397·6	−1·9	Hg₅₇₈₀	399·5	+1·0	400·5	,,
,,	373·1	−0·3	Na₅₈₉₃	373·4	−0·3	373·1	,,
,,	332·8	+1·7	Li₆₁₀₄	331·1	−0·2	330·9	,,
,,	279·5	+0·5	Cd₆₄₃₈	279·0	+0·9	279·9	,,
,,	247·1	+0·8	Li₆₇₀₈	246·3	−0·1	246·2	,,

TABLE XII.

p-Nitroanilinomethylenecamphor in methyl alcohol.

$$[\alpha] = \pm \frac{77 \cdot 47}{\lambda^2 - 0 \cdot 1470} \; ; \; \lambda_0 = 0 \cdot 3834.$$

Dextro.						Laevo.	
Conc (g./100 c.c)	Obs. [α] o.	o−c	Line	Calc. [α]. c.	o′−c.	Obs. [α]. o′.	Conc. (g./100 c.c.)
0·4004	+624·4°	+1·2°	Ag₅₂₀₉	±623 2°	−1·9°	−621·3°	0·400ε
,,	510·7	−1·5	Hg₅₄₆₁	512·2	+0·6	512·8	,,
,,	508·3	−1·4	Ag₅₄₆₈	509·7	-∴-	—	,,
,,	415·9	+1·8	Hg₅₇₈₀	414·1	−1·1	413·0	,,
,,	386·8	−0·4	Na₅₈₉₃	387·2	+0·9	388·1	,,
,,	343·9	+0·5	Li₆₁₀₄	343·4	+0·9	344·3	,,
,,	289·7	+0·1	Cd₆₄₃₈	289·6	−0·1	289·5	,,
,,	256·1	+0·4	Li₆₇₀₆	255·7	+0·1	255·8	,,

TABLE XIII.

p--Nitroanilinomethylenecamphor in acetone.

$$[\alpha] = \pm \frac{74 \cdot 11}{\lambda^2 - 0 \cdot 1556} \; ; \; \lambda_0 = 0 \cdot 3945.$$

Dextro.						Laevo.	
Conc. (g./100 c.c.)	Obs.[α]. o.	o—c.	Line.	Calc.[α]. c.	o′−c.	Obs.[α]. o′.	Conc. (g./100 c.c.)
0 4024	+720·6°	+1·6°	Cd₅₀₈₅	±719·0°	+0·1°	−719·1°	0·401ε
,,	642·4	+1·8	Ag₅₂₀₉	640·6	±0	640·6	,,
	519·4	−0·3	Hg₅₄₆₁	519·7	±0	519·7	,,
,,	415·0	−0·3	Hg₅₇₈₀	415·3	+0·9	416·2	,,
,,	385·2	−1·9	Na₅₈₉₃	387·1	−0·7	386·4	,,
	340·5	−1·0	Li₆₁₀₄	341·5	±0·0	341·5	,
,,	284·5	−1·8	Cd₆₄₃₈	286·3	+0·3	286·6	,,
,,	252·3	+0·5	Li₆₇₀₆	251·8	+1·2	253·0	,,

TABLE XIV.

p-*Nitroanilinomethylenecamphor in pyridine.*

$$[a] = \pm \frac{79 \cdot 58}{\lambda^2 - 0 \cdot 1526} \; ; \; \lambda_0 = 0 \cdot 3906.$$

Dextro.						Laevo.		
Conc. (g./100 c.c.)	Obs.[a]. o	o—c.	Line.	Calc.[a]. c.	o'—c.	Obs [a] o'.	Conc. (g./100 c.c.)
0·4028	+671·6°	+1·2°	Ag$_{5209}$	±670·4°	+1·2°	−671·6°	0·4020
,,	545·0	−1·7	Hg$_{5461}$	546·7	−0·6	546·1	,,
	542·5	−1·1	Ag$_{5468}$	543·6			,,
,,	438·2	−0·2	Hg$_{5780}$	438·4	+0·6	439·0	,,
,,	407·9	−1·3	Na$_{5893}$	409·2	−1·2	408·0	,,
,,	361·3	−0·4	Li$_{6104}$	361·7	+0·2	361·9	,,
,,	304·2	+0·3	Cd$_{6438}$	303·9	+0·8	304·7	,,
,,	268·1	+0·6	Li$_{6708}$	267·5	−0·1	267·4	,,

TABLE XV.

p-*Nitroanilinomethylenecamphor in benzene.*

$$[a] = \pm \frac{68 \cdot 05°}{\lambda^2 - 0 \cdot 1424} \; ; \; \lambda_0 = 0 \cdot 3774.$$

Dextro.				
Conc. (g$_s$/100 c.c.)	Obs.[a]. o.	o—c.	Line.	Calc.[a]. c.
0·4016	+585·2°	+0·1°	Cd$_{5085}$	±585·1
	529·1	+1·3	Ag$_{5209}$	527·8
	437·0	+0·2	Hg$_{5461}$	436·8
,,	354·8	−0 2	Hg$_{5780}$	355·0
,,	331·2	−1·2	Na$_{5893}$	332·4
,,	297·6	+1·9	Li$_{6104}$	295·7
,,	249 0	−1·0	Cd$_{6438}$	250·0
	221·6	+0·4	Li$_{6708}$	221·2

TABLE XVI.

o-Carboxyphenylaminomethylenecamphor in chloroform.

$$[\alpha] = \pm \frac{69.02}{\lambda^2 - 0.1180} \; ; \; \lambda_0 = 0.3435$$

Dextro.					Laevo.		
Conc.	Obs[α].	o—c.	Line.	Calc.[α]	o′—c.	Obs.[α].	Conc.
(g./100 c.c.)	o.			c.		o′.	(g./100 c.c.)
0·4016	+490·6°	+0·1°	Cd$_{5085}$	±490·5°	+0·7°	−491·2°	0·4000
,,	449·4	−0·7	Ag$_{5209}$	450·1	+1·1	451·2	,,
,	382·2	−0·7	Hg$_{5461}$	382·9	−0·5	382·4	,,
,,,	318·7	−0·6	Hg$_{5780}$	319·3	+0·7	320·0	,,
	301·3	+0·1	Na$_{5893}$	301·2	±0·0	301·2	,,
,..	270·2	−0·9	Li$_{6104}$	271·1	+0·2	271·3	,,
,	234·1	+1·3	Cd$_{6438}$	232·8	−0·3	232·5	,,
,	207·9	±0	Li$_{6708}$	207·9	−1·6	206·3	,,

TABLE XVII.

o-Carboxyphenylaminomethylenecamphor in pyridine.

$$[\alpha] = \pm \frac{69.89}{\lambda^2 - 0.1165} \; ; \; \lambda_0 = 0.3413.$$

Dextro.					Laevo.		
Conc.	Obs.[α].	o—c.	Line.	Calc.[α].	o′—c.	Obs.[α].	Conc.
(g./100 c.c.)	o.			c.		o′.	(g./100 c.c.)
0·4000	+483·8°	−0·6°	Cd$_{5085}$	±484·4°	−1·3°	−483·1°	0·4016
,,	446·3	+1·4	Ag$_{5209}$	444·9	−2·9	442·0	,,
,,	377·5	−1·6	Hg$_{5461}$	379·1	−0·6	378·5	,,
,,	317·5	+1·0	Hg$_{5780}$	316·5	−0·3	316·2	,,
,,	298·7	±0·0	Na$_{5893}$	298·7	+0·1	298·8	,,
,,	270·1	+1·2	Li$_{6104}$	268·9	+1·3	270·2	,,
,,	232·5	+1·3	Cd$_{6438}$	231·2	+0·4	231·6	,,
,,	206·3	−0·2	Li$_{6708}$	206·5	+0·2	206·7	

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TABLE XVIII.

o-Carboxyphenylaminomethylenecamphor in acetone.

$$[\alpha] = \pm \frac{68 \cdot 39}{\lambda^2 - 0 \cdot 1144}, \ \lambda_0 = 0 \cdot 3382.$$

Dextro.					Laevo.		
Conc. (g./100 c.c.)	Obs.[α]. o.	o—c.	Line.	Calc.[α]. c.	o'—c.	Obs.[α]. o'.	Conc. (g./100 c.c.)
0·4004	+473·3°	−0·7°	Cd$_{5085}$	±474·0°	−0·9°	−473·1°	0·4016
,,	437·1	+1·2	Ag$_{5209}$	435·9	−0·1	435·8	,,
,,	373·5	+1·5	Hg$_{5461}$	372·0	+0·4	372·4	,,
,,	311·0	−0·3	Hg$_{5780}$	311·3	−2·5	308·8	,,
,,	294·7	+0·8	Na$_{5893}$	293·9	−1·3	292·6	,,
,,	266·1	+1·1	Li$_{6104}$	265·0	+0·3	265·3	,,
,,	228·6	+0·7	Cd$_{6438}$	227·9			,,
,,	203·5	−0·3	Li$_{6708}$	203·8	−2·1	201·7	,,

TABLE XIX.

o-Carboxyphenylaminomethylenecamphor in benzene.

$$[\alpha] = \pm \frac{70 \cdot 53}{\lambda^2 - 0 \cdot 1197}; \ \lambda_0 = 0 \cdot 3460$$

Dextro.					Laevo.		
Conc. (g./100 c.c.)	Obs. [α]. o.	o—c.	Line.	Calc.[α]. c.	o'—c.	Obs. [α]. o'.	Conc. (g./100 c.c.)
0·4008	+506·5°	−0·9°	Cd$_{5085}$	±507·4°	+0·2°	−507·6°	0·4020
,,	465·4	+0·2	Ag$_{5209}$	465·2	−1·2	464·0	,,
,,	395·6	+0·4	Hg$_{5461}$	395·2	+0·3	395·5	,,
,,	329·4	+0·3	Hg$_{5780}$	329·1	+0·5	329·6	,,
,,	309·4	−0·7	Na$_{5893}$	310·1	−0·4	309·7	,,
,,	279·5	+0·6	Li$_{6104}$	278·9	−0·2	278·7	,
,,	239·5	+0·2	Cd$_{6438}$	239·3	+0·8	240·1	,,
,,	213·3	−0·2	Li$_{6703}$	213·5	+0·5	214·0	,,

TABLE XX.

o-Carboxyphenylaminomethylenecamphor in ethyl alcohol.

$$[\alpha] = \pm \frac{69.5}{\lambda^2 - 0.1199}\ ;\ \lambda_0 = 0.3463.$$

	Dextro.				Laevo.		
Conc. (g./100 c.c.)	Obs. [α]. o.	o−c.	Line.	Calc. [α]. c.	o'−c.	Obs. [α]. o'.	Conc. (g./100 c.c.)
0.4004	+629.4°	+0.3°	Cd4800	±629.1°	—	—	0.4000
,,	502.0	+1.3	Cd5085	500.7	−0.7°	−500.0°	,,
,,	458.2	−0.9	Ag5209	459.1	+0.8	459.9	,,
,,	388.5	−1.2	Hg5461	389.7	+0.3	390.0	,,
,,	324.7	+0.2	Hg5780	324.5	+0.5	325.0	,,
,,	304.7	−1.2	Na5893	305.9	+1.6	307.5	,,
,,	273.5	−1.6	Li6104	275.1	−1.4	273.7	,,
,,	236 0	+0.1	Cd6438	235.9	+0.4	236.3	,,
,,	211.1	±0.0	Li6708	211.1	−0.2	211.3	,,

TABLE XXI.

o-Carboxyphenylaminomethylenecamphor in methyl alcohol.

$$[\alpha] = \pm \frac{69.45}{\lambda^2 - 0.1204}\ ;\ \lambda_0 = 0.3470.$$

	Dextro.				Laevo.		
Conc. (g./100 c.c.)	Obs. [α]. o.	o−c.	Line.	Calc. [α]. c.	o'−c.	Obs. [α] o'.	Conc. (g./100 c.c.)
0.4024	+503.2°	+1.1°	Cd5085	±502.1°	+0.2°	−502.3°	0.4012
,,	459.7	−0.6	Ag5209	460.3	+0.9	461.2	,,
,,	388.9	−1.6	Hg5461	390.5	−0.4	390.1	,,
,,	324.3	−0.7	Hg5780	325.0	+0.3	325.3	,,
,,	306.9	+0.6	Na5893	306.3	+0.3	306.6	,,
,,	274.6	−0.8	Li6104	275.4	+0.1	275.5	,,
,,	236.1	−0.1	Cd6438	236.2	−0.6	235.6	,,
,,	211.2	+0.5	Li6708	210.7	±0.0	210.7	,,

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TABLE XXII.

m-*Carboxyphenylaminomethylenecamphor in pyridine.*

$$[a] = \pm \frac{67 \cdot 57}{\lambda^2 - 0 \cdot 1163} \; ; \; \lambda_0 = 0 \cdot 3410.$$

Dextro.						Laevo.		
Conc. (g./100 c.c.)	Obs. [a]. o.	o—c.	Line.	Calc. [a]. c.	o'—c	Obs. [a]. o'.	Conc. (g./100 c.c.
0·4024	+593·9°	+1·6°	Cd$_{4800}$	±592·3°	—	—	0·4012
,,	474·4	—0·1	Cd$_{5085}$	474·5	—2·1°	—472·4°	,,
,,	436·1	+0·1	Ag$_{5209}$	436·0	+0·3	436·3	,,
,,	371·5	±0·0	Hg$_{5461}$	371·5	—0·1	371·4	,,
,,	310·6	+0·4	Hg$_{5780}$	310·2	+0·1	310·3	,,
,,	293·2	+0·4	Na$_{5893}$	292·8	+0·2	293·0	,,
,,	263·4	—0·3	Li$_{6104}$	263·7	—0·7	263·0	,,
,,	227·4	+0·7	Cd$_{6438}$	226·7	+0·2	226·9	,,
,,	202·5	±0·0	Li$_{6708}$	202·5	—0·5	202·0	,,

TABLE XXIII.

m-*Carboxyphenylaminomethylenecamphor in acetone.*

$$[a] = \pm \frac{68 \cdot 3}{\lambda^2 - 0 \cdot 1165}, \; \lambda_0 = 0 \cdot 3413$$

Dextro.						Laevo.		
Conc. (g./100 c.c.)	Obs. [a]. o.	o—c.	Line.	Calc. [a] c.	o'—c.	Obs. [a] o'.	Conc. (g./100 c.c)
0·4028	+600·9°	+1·4°	Cd$_{4800}$	±599·5°			0·4016
,,	480·4	+0·1	Cd$_{5085}$	480·3	+0·4°	—480·7°	,,
,,	441·9	+0·7	Ag$_{5209}$	441·2	+0·8	442·0	,,
,,	376·1	+0·2	Hg$_{5461}$	375·9	+1·4	377·3	,,
,,	314·8	+1·0	Hg$_{5780}$	313·8	+1·2	315·0	,,
,,	295·4	—0·8	Na$_{5893}$	296·2	—1·1	295·1	,,
,,	266·9	+0·2	Li$_{6104}$	266·7	—1·4	265·3	,,
,,	229·7	+0·5	Cd$_{6438}$	229·2	—0·1	229·1	,,
,,	204·8	±0·0	Li$_{6708}$	204·8	—0·6	204·2	,,

TABLE XXIV.

m-*Carboxyphenylaminomethylenecamphor in ethyl alcohol.*

$$[a] = \pm \frac{70 \cdot 33}{\lambda^2 - 0 \cdot 1180}; \ \lambda_0 = 0 \cdot 3435.$$

Dextro.						Laevo.	
Conc. (g./100 c.c.)	Obs. [a]. o.	o−c.	Line.	Calc· [a]. c.	o′−c	Obs. [a]. o′.	Conc. (g./100 c.c.)
0·4016	+499·2°	−0·5°	Cd$_{5085}$	±499·7°	+0·3°	−500·0°	0·4020
,,	458·1	−0·5	Ag$_{5209}$	458·6	+0·4	459·0	,,
,,	390·9	+0·7	Hg$_{5461}$	390·2	+0·3	390·5	,,
,,	324·9	−0·5	Hg$_{5780}$	325·4	+0·5	325·9	,,
,,	307·5	+0·5	Na$_{5893}$	307·0	−1·0	306·0	,,
,,	276·5	+0·2	Li$_{6104}$	276·3	−0 1	276·2	,,
,,	237·8	+0·6	Cd$_{6438}$	237·2	−0·8	236·4	,,
,,	211·6	−0·2	Li$_{6708}$	211·8	+1·0	212·8	,,

TABLE XXV.

m-*Carboxyphenylaminomethylenecamphor in methyl alcohol.*

$$[a] = \pm \frac{70 \cdot 62}{\lambda^2 - 0 \cdot 1202}; \ \lambda_0 = 0 \cdot 3467.$$

Dextro.						Laevo.	
Conc. (g./100 c.c.)	Obs. [a]. o.	o−c.	Line.	Calc. [a]. c.	o′−c.	Obs. [a]. o′.	Conc. (g./100 c.c.)
0·4020	+509·9°	+0·1°	Cd$_{5085}$	±509·8°	−0·6°	−509·2°	0·4016
,,	466·3	−1·0	Ag$_{5209}$	467·3	+0·9	468·2	,,
,,	396·8	±0·0	Hg$_{5461}$	396·8	+0·4	397·2	,,
,,	329·6	−0·5	Hg$_{5780}$	330·1	+1 1	331·2	,,
,,	310·9	−0·4	Na$_{5893}$	311·3	−0·1	311·2	,,
,,	279·9	+0·1	Li$_{6104}$	279·8	−0·9	278·9	,,
,,	241·3	+1·3	Cd$_{6438}$	240·0	+0·3	240 3	,,
,	213·9	−0·2	Li$_{6708}$	214·1	±0·0	214·1	,,

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TABLE XXVI.

p-Carboxyphenylaminomethylenecamphor in pyridine.

$$[\alpha] = \pm \frac{74.78}{\lambda^2 - 0.1229}; \ \lambda_0 = 0.3506.$$

Dextro.						Laevo.		
Conc. (g./100 c.c.)	Obs. [α]. o.	o—c.	Line.	Calc [α] c.	o'—c.	Obs. [α]. o'.	Conc. (g./100 c.c.)
0.4000	+550·0°	—0·8°	Cd$_{5085}$	±550·8	—1·2°	—549·6°	0.4012
,,	505·1	+1·2	Ag$_{5209}$	503·9	—1·6	502·3	,,
,,	426·3	—0·4	Hg$_{5461}$	426·7	—0·4	426·3	,,
,,	353·8	—0·3	Hg$_{5780}$	354·1	—0·1	354·0	,,
,,	335·0	+1·4	Na$_{5893}$	333·6	+0·5	334·1	,,
,,	300·0	+0·5	Li$_{6104}$	299·5	—2·8	296·7	,,
,,	256·3	—0·1	Cd$_{6438}$	256·4	+0·4	256·8	,,
,,	228·8	+0·1	Li$_{6708}$	228·7	+0·6	229·3	,,

STEREOCHEMISTRY OF MONOCYCLIC RINGS. PART I. INTERCONVERSION OF METHYLCYCLOHEXANE INTO METHYLCYCLOHEPTANE RING AND SYNTHESIS OF 4-METHYLCYCLOHEPTANONE.

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4-Methylcycloheptanone has been synthesised by three different methods. Firstly 4-methylcyclohexanonecyanohydrin was converted into 4-methylcyclohexenyl cyanide which was reduced to 4-methylcyclohexylmethylamine and di-4-methylcyclohexylmethyl-amine. Distillation of the product obtained by the action of nitrous acid on the primary amine, yielded 4-methylcycloheptene, 4-methylcycloheptanol and 4-methylcyclohexyl-carbinol. 4-Methylcycloheptanol on being oxidised gave a ketone mixture from which it has been inferred that 4-methylcycloheptanone exists in isomeric forms.

Methylsuccinic ester gave a diol on reduction which was subsequently converted into the dibromide, the di-nitrile and methyladipic acid. By the action of sodio-malonic ester on the dibromide and the subsequent hydrolysis, the corresponding suberic acid could not be obtained. The only product of this reaction was methylcyclopentane carboxylic acid. The methyladipic acid was, however, more conveniently prepared by the oxidation of 4-methylcyclohexanone. This was converted into the diol, di-bromide, di-nitrile and γ-methylsuberic acid without much difficulty.

By a third method pure 4-methylcyclohexanone was converted into a mixture of ketones by the action of diazomethane by the method of Mosettig and Burger. From the ketone mixture, the semicarbazone of 4-methylcycloheptanone was isolated in fairly good yield.

It appeared to be of interest to examine the condition under which a a particular ring structure can be interconverted into some other ring, the formation of which is more difficult according to Baeyer's hypothesis. Demjanow reaction provides an important experimental method for changing a lower ring system into the next higher. From the relative ease of forma-tion of such rings, a rough estimate of the amount of strain may perhaps be made, particularly if no other factors influence such ring transformation. The preparation of substituted higher ring compounds has an added in-terest in that there is a possibility of isolating the necessary number of isomers if the ring system is multiplanar in character. With these ideas in view, methylcyclohexane ring was subjected to Demjanow change in order to isolate the related methylcycloheptane-derivative.

The method of Ruzicka and Brugger (*Helv. Chim. Acta*, 1926, **9**, 319) offers a possibility of transforming methylcyclohexane into a methlcyclohep-tane ring. Accordingly *p*-methylcyclohexanone was chosen as the first

substance to be employed, as this will not present the difficulties of forming more than one structural isomer by its ultimate transformation. Pure *p*-methyl*cyclo*hexanone was converted into the cyanohydrin (I) through the bisulphite compound and potassium cyanide, or by the direct addition of hydrogen cyanide to the free ketone The cyanohydrin (I) was dehydrated by thionyl chloride to unsaturated nitrile (II), Ruzicka's method (*loc. cit.*) proving more satisfactory than that of Darzen (*Compt. rend.*, 1911, **152**, 1601).

$$CH_3 \cdot CH \begin{array}{c} CH_2-CH_2 \\ CH_2-CH_2 \end{array} C \begin{array}{c} OH \\ CN \end{array} \qquad CH_3 \cdot CH \begin{array}{c} CH_2-CH \\ CH_2-CH_2 \end{array} C \cdot CN$$

<div align="center">(I)   (II)</div>

$$CH_3 \cdot CH \begin{array}{c} CH_2-CH_2 \\ CH_2-CH_2 \end{array} CH \cdot CH_2 \cdot NH_2$$

<div align="center">(III)</div>

The reduction of the unsaturated nitrile furnished the amine (III) together with a small quantity of di-*p*-methyl*cyclo*hexylmethylamine as a by-product. The separation of these two amines was effected by distillation. The amine (III) was characterised by the formation of monobenzoyl derivative, a picrate, and other derivatives.

The primary amine (III) with nitrous acid gave a mixture of three different compounds, which were separated by careful fractional distillation. The lowest boiling fraction was the hydrocarbon (IV), while the middle fraction, which constituted the major portion of the mixture, consisted of 4-methyl*cyclo*heptanol (V). The highest fraction was obtained in very small quantity and this could not be thoroughly examined. It may perhaps be *p*-methyl*cyclo*hexylcarbinol.

$$CH_3 \cdot CH \begin{array}{c} CH_2-CH_2-CH \\ \quad \| \\ CH_2-CH_2-CH \end{array} \qquad CH_3 \cdot CH \begin{array}{c} CH_2-CH_2-CH \cdot OH \\ \quad | \\ CH_2-CH_2-CH_2 \end{array}$$

<div align="center">(IV)   (V)</div>

The alcohol (V), when oxidised with chromic acid, gave a ketone mixture, which yielded a semicarbazone of indefinite melting point. By careful crystallisation this was separated into two fractions, one melting at 159° and the other at 124°. The second semicarbazone (m. p. 124°) was not obtained in sufficient amount for a thorough examination. We are,

therefore, unable at present to pronounce it to be a semicarbazone of an isomeric methyl*cyclo*heptanone (VI) or that of an aldehyde obtained from *p*-methyl*cyclo*hexylcarbinol which might have been present in small quantity in the alcohol (V) The alcohol (V), however, was converted into a solid hydrogen phthalic ester and the sample used for oxidation was regenerated from the hydrogen phthalate. Therefore, we are inclined to the view that the isomeric semicarbazone could not be that of an aldehyde (VII) and is most probably an isomeric *cyclo*heptanone. We are now investigating this point more fully.

$$CH_3 \cdot CH \Big\langle {\substack{CH_2-CH_2-CO \\ | \\ CH_2-CH_2-CH_2}} \qquad CH_3\,CH \Big\langle {\substack{CH_2-CH_2 \\ CH_2-CH_2}} \Big\rangle CH \cdot CHO$$

$$(VI) \qquad\qquad\qquad (VII)$$

In order to establish the identity of 4-methyl*cyclo*heptanone, thus prepared, it was considered necessary to synthesise the ketone. For this purpose, we at first thought that ethyl α-methylsuccinate might be reduced to the diol (VIII, R = OH). Its dibromide (VIII, R = Br) should give ethyl 3-methylhexane-1:1:6:6-tetracarboxylate (IX), which would yield γ-methyl-suberic acid on hydrolysis.

$$\substack{CH_3 \cdot CH-CH_2R \\ | \\ CH_2-CH_2R} \qquad \substack{CH_3CH \cdot CH_2 \cdot CH \big\langle {\substack{CO_2Et. \\ CO_2Et}} \\ | \\ CH_2 \cdot CH_2 \cdot CH \big\langle {\substack{CO_2Et \\ CO_2Et}}}$$

$$(VIII) \qquad\qquad\qquad (IX)$$

But the dibromide (VIII, R = Br) gave ethyl 3-methyl*cyclo*pentane-1:1-dicarboxylate (X) exclusively with sodiomalonic ester. The product is hydrolysed to 3-methyl*cyclo*pentane-1-carboxylic acid.

$$CH_3 \cdot CH \Big\langle {\substack{CH_2-C(CO_2Et)_2 \\ | \\ CH_2-CH_2}}$$

$$(X)$$

β-Methyladipic acid, prepared by the oxidation of *p*-methyl*cyclo*hexanone was identical with the acid obtained by the hydrolysis of the dinitrile (VIII, R = CN) prepared from the corresponding dibromide.

Ethyl β-methyladipate furnished the diol (XI, R=OH) on reduction. This was then converted *via* the dibromo derivative to the dinitrile (XI, R=CN).

$$CH_3 \cdot CH \Big\langle \begin{array}{c} CH_2\!-\!CH_2 \cdot CH_2R \\ CH_2\!-\!CH_2R \end{array}$$

(XI)

The nitrile was hydrolysed to γ-methylsuberic acid (XI, R=COOH) and thence to 4-methyl*cyclo*heptanone.

The ketone has also been prepared by the action of diazomethane on p-methyl*cyclo*hexanone in the presence of methyl alcohol and potassium hydroxide. During this reaction the intermediate compound (XII) changed partially into the oxide (XIII), which has not been isolated. But methyl*cyclo*octanone was obtained in small quantity, while methyl*cyclo*heptanone (VI) was the main product of this reaction (*cf.* Mosettig and Burger, *J. Amer. Chem. Soc.*, 1930, **52**, 3456). The separation of these two ketones was effected by fractional crystallisation of their semicarbazones.

$$CH_3 \cdot CH \Big\langle \begin{array}{c} CH_2\!-\!CH_2 \\ CH_2\!-\!CH_2 \end{array} \!\!\Big\rangle C\!-\!\!-\!\!-\!CH_2 \qquad CH_3 \cdot CH \Big\langle \begin{array}{c} CH_2\!-\!CH_2 \\ CH_2\!-\!CH_2 \end{array} \!\!\Big\rangle C\!-\!\!-\!CH_2$$

(XII)   (XIII)

The synthetic ketones, obtained by the two above described methods, yielded primarily one semicarbazone which was identical with that obtained in greater quantity from the ketone prepared by Demjanow method.

EXPERIMENTAL.

*4-Methyl-1-cyano-1-hydroxy*cyclohexane (I).—A solution of sodium bisulphite (104 g., 1 mol.) in water (140 c.c.), cooled in ice, was saturated with sulphur dioxide. To the ice-cold solution, p-methyl*cyclo*hexanone (56 g., ½ mol.) was added gradually with continuous stirring and then left overnight. The bisulphite compound was collected, washed successively with rectified spirit and a little ether. The paste of the bisulphite compound with a little water, cooled in ice, was gradually treated with a solution of potassium cyanide (65 g.) in water (110 c.c.) with vigorous shaking. After standing for 2 hours at 0°, the oily product was filtered from the crystalline solid which was very carefully washed with ether. From the filtrate the oily

layer of cyanohydrin was separated and the aqueous solution repeatedly extracted with ether. The combined extracts were dried and the solvent was removed after the addition of a few drops of concentrated sulphuric acid. The residual liquid was fractionated and the cyanohydrin collected at 65-68°/5 mm., yield 51 g. (72%). (Found: C, 68·82; H, 8·9. $C_8H_{13}ON$ requires C, 69·06; H, 9·3 per cent). This on keeping in a glass container underwent decomposition and hydrogen cyanide was slowly evolved and the decomposition was rapid in presence of ammonia.

The cyanohydrin may also be prepared by the action of hydrogen cyanide but the product is not so pure. *p*-Methyl*cyclo*hexanone (56 g., ½ mol.) was gradually added to the liquid hydrogen cyanide (33 c.c.), cooled in a freezing mixture and then a few drops of dimethylaniline added and the mixture left overnight. After the removal of unreacted hydrogen cyanide in vacuum, the mixture was dissolved in ether, washed with a dilute solution of hydrochloric acid and after removal of the solvent, the residual oil fractionated. The first fraction consisted of unreacted ketone (4 g.) and the second fraction gave the cyanohydrin (58 g., 81%).

4-Methyl-Δ¹-cyclohexenyl Cyanide (II).—(*a*) A solution of 4-methyl-1-cyano-1-hydroxy*cyclo*hexane (50 g.) in dry benzene (60 c.c.), cooled in a freezing mixture, was mixed with thionyl chloride (100 g.) dropwise with continuous stirring during 1½ hours and then left overnight. After being gently warmed on a water-bath for 2 hours, the cooled mixture was decomposed with ice-water (75 c.c.). The benzene extract of the unsaturated nitrile was washed with dilute sodium carbonate solution, dried, freed from the solvent and the residual oil fractionated, when 2·5 g. of the unreacted cyanohydrin were recovered at 65-68°/5 mm. and the unsaturated nitrile (30 g.) boiled at 98-100°/5 mm. After repeated fractionation the unsaturated nitrile was obtained as a colourless mobile liquid, which had d_4^{32}, 0·93954; n_D^{32}, 1·46898; whence $[R_L]_D$, 35·9 (calc. 36·2). (Found: C, 79·0; H, 8·8. $C_8H_{11}N$ requires C, 79·3; H, 9·0 per cent).

(*b*) The dehydration was also effected by Darzen's method but less satisfactorily. To a mixture of crude cyanohydrin (50 g.) in pyridine (79 g., 1 mol.), cooled in ice, thionyl chloride (131 g., 1·1 mol.) was added dropwise with continuous stirring during 1 hour. The dark product was heated under reflux for 1 hour, poured into water and acidified. After filtration it was extracted with ether, the ethereal extract washed with sodium hydroxide solution (5%), dried and on repeated fractionation afforded 25 g. of the pure unsaturated nitrile.

(i) *Partial Hydrolysis of the Unsaturated Nitrile* (II) *to the corresponding Amide.*—To the ice-cold nitrile (2 g.) was added drop by drop ice-cold sulphuric acid (d 1·84, 1 c.c.) and after standing at the room temperature for 24 hours, the mixture was heated on a steam-bath for 10 hours. The thick mass after decomposition with crushed ice was extracted repeatedly with ether, the extract washed with sodium carbonate solution, dried over sodium sulphate and the solvent removed. The yellowish residue crystallised from methyl alcohol, and had m.p. 140°. (Found: C, 68·7 ; H, 9·1. $C_8H_{13}ON$ requires C, 69·06 ; H, 9·3 per cent).

(ii) The complete hydrolysis of the unsaturated nitrile to Δ^1-tetrahydro-p-toluic acid was effected by heating it under reflux for 10 hours with concentrated hydrochloric acid. The acid after isolation in the usual manner crystallised from alcohol, m.p. 132-33°. (Found : C, 68·4 ; H, 8·5. $C_8H_{12}O_2$ requires C, 68·57 ; H, 8·57 per cent).

p-*Methylcyclohexylmethylamine* (III).—A solution of p-methylcyclohexenyl cyanide (20 g.) in amyl alcohol (dried over calcium) was heated to boiling and to the hot solution sodium (30 g.) was added portionwise and the reaction was allowed to proceed as vigorously as was consistent with safety. The temperature was then gradually raised to 160-70° and heating continued till all the sodium dissolved (4 hrs.). It was then allowed to cool, but while still hot, a little water (50 c.c.) was gradually introduced to prevent solidification of the mass. The solution was cooled in ice and then gradually acidified with 300 c.c. of hydrochloric acid (d 1·15). After removal of amyl alcohol with steam, the residual solution containing sodium chloride and the hydrochloride of the amine was evaporated to dryness on a steam-bath. The residue was powdered and treated with ether. It was then treated with an excess of well-cooled solution of potassium hydroxide (20 g.) in water (100 c.c.). The liberated amine was extracted three times with ether. The ethereal extract was dried at first over potassium hydroxide and then over anhydrous potassium carbonate. After removal of the solvent the residual liquid was fractionated. The first fraction, b.p. 67-80°/30-35 mm. (2 g.) was the unsaturated nitrile. The second fraction, which had b.p. 85-98°/34-35 mm. was a colourless liquid (10·5 g.). (Found : C, 75·9 ; H, 13·31. $C_8H_{17}N$ requires C, 75·6 ; H, 13·38 per cent). It had d_4^{31}, 0·85481 ; n_D, 1·45537 ; whence $[R_L]_D$, 40·32 (calc. 40·36).

The *benzoyl derivative* of the amine, prepared in the usual manner, crystallised from ethyl alcohol, m.p. 93°. (Found: C, 77·4; H, 8·8. $C_{15}H_{21}ON$ requires C, 77·9 ; H, 9·09 per cent).

The *platinum compound*, prepared in the usual manner, crystallised from rectified spirit in well defined rhombohedra, m.p. 248° (decomp.). (Found : Pt, 29·33. $C_{16}H_{36}N_2Cl_6Pt$ requires Pt, 29·36 per cent),

The hydrochloride crystallised from methyl alcohol in beautiful shining needles, m.p. 248-50° (with shrinking from 220° and decomposition). (Found : Cl, 21·42. $C_8H_{17}N$, HCl requires Cl, 21·7 per cent).

The third fraction, b.p. 155-165°/30-35 mm. (3 g.) probably consisted of di-p-methylcyclohexylmethylamine, which was obtained as a thick liquid having d_4^{33}, 0·86377.; n_D, 1·45597; whence $[R_L]_D$, 74·6 (calc. 75). (Found : C, 80·5 ; H, 12·7. $C_{16}H_{31}N$ requires C, 81·0; H, 13·1 per cent).

4 Methylcycloheptanol and 4-Methylcycloheptene.—The solution of p-methylcyclohexylmethylamine (20 g.) in glacial acetic acid (11 c.c.) and water (100 c.c.) was very slowly treated with a solution of sodium nitrite (11 g.) in 12 c.c. of water. The mixture was shaken well and then heated on the steam-bath for 1½ hours with an efficient condenser through which ice-water was circulated. The brown oil separating on the surface was taken up in ether. The ethereal solution was washed with sodium carbonate solution and then with water and finally dried over anhydrous sodium sulphate. After removal of the solvent the residual oil was carefully distilled and three fractions were collected : (*i*) b.p. 65-72°/38-40 mm. or 110-20°/90 mm. (yield 3·5 g.); (*ii*) b.p. 102-5°/32-35 mm. or 125-130°/90 mm. (yield 11g.) ; (*iii*) b.p. 170-208°/14 mm. or 165-75°/7 mm. (yield 1·5 g.).

The aqueous acetate mother-liquor was made alkaline and the unreacted amine (3 g.) was regenerated.

4-Methylcycloheptene (V).—The fraction (*i*) was identified to be 4-methylcycloheptene. It absorbed bromine in carbon disulphide solution. It was purified by redistilling over sodium at 69-70°/38 mm. and had d_4^{31}, 0·76061 ; n_D^{31}, 1·42016 ; whence $[R_L]_D$, 36·2 (calc. 36·48). (Found : C, 87·0 ; H, 12·54. C_8H_{14} requires C, 87·27 ; H, 12·7 per cent).

γ-Methylpimelic Acid from 4-Methylcycloheptene.—The unsaturated hydrocarbon (3 g.) was oxidised with potassium permanganate (10 g.) in water (500 c.c.) by the usual method when γ-methylpimelic acid was obtained which, when crystallised from dry ether, had m.p. 56°. (Found : C, 54·9 ; H, 8·1. $C_8H_{14}O_4$ requires C, 55·17 ; H, 8·04 per cent).

4-Methylcycloheptanol (VI).—The second fraction, b.p. 102-105°/32-35 mm. was identified as 4-methylcycloheptanol by its conversion into the corresponding hydrogen phthalate. Equal weights of alcohol and finely powdered phthalic anhydride were mixed with little dry benzene and heated for several hours on the steam-bath under reflux. The mixture was then poured into crushed ice, sodium carbonate solution was added in slight excess and the insoluble portion removed. The filtrate was acidified with dilute sulphuric acid, extracted with ether, dried and the solid residue, obtained after removal of the solvent, was purified by several crystallisations

4

from light petroleum. It crystallises in silver white leaflets, m.p. 95-97°. (Found: C, 70·6; H, 7·58. $C_{16}H_{20}O_4$ requires C, 69·6 ; H, 7·24 per cent). It is readily soluble in alcohol or ether, sparingly soluble in light petroleum and insoluble in water. Methyl*cyclo*heptanol regenerated from the hydrogen phthalate had, b.p. 105-106°/39-40 mm., $d_4^{31·8}$, 0·91338; n_D, 1·45737 ; whence $[R_L]_D$, 38·2 (calc. 38·4. (Found : C, 74·61 ; H, 12·49. $C_8H_{16}O$ roquires C, 75·0 ; H, 12·5 per cent.

*4-Methyl*cyclo*heptanone.*— 4-Methyl*cyclo*heptanol (10 g.), purified through its hydrogen phthalate,. was dissolved in glacial acetic acid (30 c.c.) and cooled in a freezing mixture. A solution of chromic acid (6·8 g.) in water (10 c.c.) was slowly added and the reaction was allowed to proceed for 10 days at the room temperature, the mixture being shaken occasionally. It was then diluted with water and extracted with ether. The ethereal solution after washing with sodium carbonate solution was dried, the solvent removed and the residue distilled and the fraction, b.p. 110-12°/55 mm. was collected. The semicarbazone of the ketone was crystallised from methyl alcohol when it melted indefinitely between 151-56°. By careful fractional crystallisation of the semicarbazone two samples were ultimately separated, one in very large proportion, m.p. 159° (sharp). (Found : C, 58·68; H, 9·14. $C_9H_{17}ON_3$ requires C, 59·01 ; H, 9·29 per cent) and the other in small proportion, m.p. 124°.

The ketone regenerated from the semicarbazone, m.p. 159°, possesses distinct camphoraceous odour and had d_4^{32}, 0·90178; n_D^{32}, 1·44385 ; whence $[R_L]_D$, 36·8 (calc. 36·95). (Found : C, 75·9 ; H, 10·7. $C_8H_{14}O$ requires C, 76·19 ; H, 11·1 per cent).

*Attempt to. Synthesise 4-Methyl*cyclo*heptanone*-—Ethyl β-methylcyano-succinate was prepared by a modification of the method of Bone and Sprankling (*J. Chem. Soc.*, 1899, **75**, 853) in better yield. Ethyl cyanoacetate (113 g , 1 mol.) was added to a well cooled solution of sodium (22 g.) in 300 c.c. of alcohol dried over calcium, when a white pasty sodium compound was formed. Ethyl α-bromopropionate (181 g., 1 mol.) was added drop by drop with vigorous stirring ; the mixture being cooled all the while. The sodium compound dissolved immediately with evolution of heat and the mixture was then heated on a water-bath for 4 hours. The solution was filtered from sodium bromide and treated with a little water and the alcohol was removed in *vacuo*. The residue was extracted with ether, the ethereal solution fractionally distilled and ethyl α-cyano-β methyl-succinate collected at 125-150°/4 mm. and then redistilled at 148-50°/4 mm., yield 165 g. (70%). (Found: C,56·08; H, 7·22. $C_{10}H_{15}O_4N$ requires C,. 56·33; H, 7·04 per cent),

Methylsuccinic Acid.—Ethyl α-cyano-β-methylsuccinate (165 g.) was re-fluxed with 5 times its volume of concentrated hydrochloric acid for 10 hours until the whole of the oil had disappeared. On cooling no acid separated. The solution was evaporated on a water-bath to dryness and the solid residue was powdered and repeatedly extracted with ether. The acid was obtained as a solid mass and then crystallised from benzene, m.p. 112°, yield 77 g (85%).

Ethyl β-Methylsuccinate.—Methylsuccinic acid (74 g.) was esterified with absolute alcohol (294 c.c.) and sulphuric acid (15 c.c.) for 6 hours. The ester, isolated in the usual manner, had b. p. 106°/11 mm., yield 93 g. (82%).

β-Methyl-aδ-butane-diol.—A solution of ethyl β-methylsuccinate (28 g.) in alcohol (200 c.c.), dried over metallic calcium, was quickly poured on to thin pieces of sodium (45 g.) from a separating funnel fitted to one arm of a Y-tube which was corked to a two litre flask. When the temperature had risen sufficiently the sodium was dispersed by shaking the contents and then the rest of alcohol (25 c.c.) was gradually poured in and the reaction allowed to proceed as vigorously as was consistent with safety. The mixture was then refluxed on an oil-bath at 140°. After addition of water (14 c.c.) the mixture was refluxed for another 30 minutes. It was then cooled in ice and hydrochloric acid (d 1·16, 207 c.c) was gradually poured in. After the removal of sodium chloride formed, the filtrate was freed from water and acid by treatment with anhydrous potassium carbonate (225 g.). The alcoholic solution was refiltered from the solid and the latter twice washed with boiling alcohol. The combined solutions of alcohol were evaporated under reduced pressure and the residual oil fractionated. The glycol (VIII, R̈=OH) had b.p. 120-22°/8 mm., yield 10 g. (60%). (Found: C, 57·6; H, 11·6. $C_5H_{12}O_2$ requires C, 57·7, H, 11·5 per cent).

β-Methyl-aδ-dibromobutane.—Pure hydrogen bromide was passed into β-methylbutane-aδ-diol (22 g.) heated on an oil-bath at 140-45°. With the gradual formation of the low-boiling dibromide, the liquid began to reflux. The gas was passed (3 hours) until it began to escape freely through the condenser. The mixture was taken up in ether and the ethereal solution washed with a little bicarbonate solution and finally with water. The oil obtained from ether was fractionated and the dibromide collected at 125-28°/55 mm., yield 25 g. (63%). (Found : Br, 69·02. $C_5H_{10}Br_2$ requires Br, 69·56 per cent). It is a heavy colourless oil possessing a sharp and unpleasant odour. It gradually darkens on exposure to air and light.

Condensation of the Dibromide with Sodiomalonic Ester.—To mole-cularised sodium (11·5 g.) and dry benzene (249 c.c.), placed in a three-necked

flask provided with a condenser, a stirrer and a tap-funnel, ethyl malonate (80 g.) was added dropwise and the mixture stirred continuously with ice-cooling. The mixture after standing in the bath for 1 hour was allowed to attain the room temperature and then heated on a water-bath for 30 minutes so as to complete the reaction. After cooling it again in ice, the dibromide (56 g.) was added drop by drop with vigorous stirring and the mixture was refluxed for 4 hours on a water-bath. The benzene solution was then washed with a little water and the aqueous layer was twice extracted with benzene. The combined benzene extracts were dried and the solvent removed in *vacuo* through a fractionating column. The almost colourless residual oil on repeated fractionation separated into two parts : one boiling at 105-115°/40-50 mm. consisting of ethyl malonate and the other at 120-22°/9-10 mm. The latter was ethyl 3-methyl*cyclo*pentane-1:1-dicarboxylate. (Found: C, 62·8; H, 8·7. $C_{12}H_{20}O_4$ requires C, 63·15; H, 8·77 per cent). It is a thick colourless oil of peculiar odour.

3-*Methyl*cyclo*pentane-1:1-dicarboxylic Acid.*—Ethyl 3-methyl*cyclo*pentane-1:1-dicarboxylate (22·8 g.) was hydrolysed with a solution of potassium hydroxide (15 g.) in water (15 c.c.) and alcohol (45 c.c.) by refluxing for 4 hours. The acid, isolated in the usual manner, was freed from traces of oil over a porous tile and then crystallised from dry ether. m. p. 117-18° (decomp.). It is soluble in water, alcohol and ether. If the concentrated ethereal solution is allowed to evaporate spontaneously, transparent plates are obtained.

The silver salt of methyl*cyclo*pentane-dicarboxylic acid was prepared in the usual manner. (Found : Ag, 55·87. $C_8H_{10}O_4Ag_2$ requires Ag, 55·9 per cent).

3-*Methyl*cyclo*pentane-1-carboxylic Acid.*— 3-Methyl*cyclo*pentane-1:1-dicarboxylic acid (8 g.) was heated at 185-200° until the evolution of carbon dioxide had ceased. The residual oily mass was thrice distilled, b. p. 92-94°/7-8 mm., yield 3 g. It is a thick colourless oil and possesses an unpleasant odour. The *silver* salt of 3-methylpentamethylene-1-carboxylic acid was prepared as usual, purified and then analysed. (Found: Ag, 45·48. $C_7H_{11}O_2Ag$ requires Ag, 45·95 per cent).

β-*Methyladiponitrile.*—The αδ-dibromo-β-methylbutane (10 g.) was mixed with finely powdered potassium cyanide (5·7 g.) in alcohol (50 c.c.) and was heated under reflux for 18 hours on a steam-bath. Alcohol was then removed very carefully under reduced pressure. The dinitrile was taken up in ether and the solid residue was also washed with ether. The dinitrile was then distilled at 140-145°/30-35 mm., yield 8 g. (80%). It was redistilled and had b.p. 138-40°/30 mm. (Found : C, 68·7 ; H, 8·05. $C_7H_{10}N_2$ requires C, 68·85 ; H, 8·2 per cent).

β-Methyladipic Acid.—(i) β-Methyladiponitrile (8 g.) was hydrolysed by heating with 6 times its volume of hydrochloric acid for 8 hours. The solution was cooled and the oily layer was taken up in ether, the ethereal solution was extracted with dilute sodium carbonate solution. The alkali washings together with the neutralised mother-liquor were evaporated to dryness. The residue was just acidified with concentrated hydrochloric acid, cooled and extracted four times with ether. From ether a brownish black thick liquid was obtained. The last traces of hydrochloric acid were freed by evaporation of its aqueous solution four times and then it was crystallised from a mixture of dry ether and petrol (1:4), m. p. 89°.

(ii) A solution (5%) of potassium permanganate (95 g.) in water (1900 c c.) was added slowly to 4-methyl*cyclo*hexanol (25 g.) with vigorous stirring during 24 hours and finally the solution was warmed on a steam-bath for 1 hour. When the colour of the permanaganate had disappeared the solution was filtered and the filtrate was evaporated to dryness and the residue was acidified. The solution together with the solid was extracted with ether after cooling. The residue from ether solidified on keeping in a vacuum desiccator. The acid was crystallised from a mixture of dry ether and petroleum when a crystalline solid, m. p. 90°, was obtained. From 100 g. of alcohol. 84 g. of the acid were obtained.

Ethyl β-methyladipate was prepared in the usual way and it boiled at 130-32°/14 mm

3-Methylhexane-1:6-diol.—The solution of ethyl β-methyladipate (43·2 g.) in alcohol (dried over metallic calcium) (200 c.c.) was quickly poured over thin pieces of sodium (60 g.), vigorous boiling ensued at once. The mixture was then heated in an oil-bath and the remaining alcohol (400 c.c.) was introduced as quickly as was consistent with safety. The rest of the reaction was carried out under experimental conditions as described in the preparation of β-methyl-αδ-butane-diol. It was obtained as a thick colourless liquid, b. p. 158-160°/15 mm., yield 16 g. (Found: C, 63·46; H, 11·9. $C_7H_{16}O_2$ requires C, 63·6 ; H, 12·1 per cent).

1:6-Dibromo-3-methylhexane.—Pure and dry hydrogen bromide was passed into the diol which was heated in an oil-bath at 140-45° with a reflux arrangement. With the gradual formation of the low-boiling dibromide the oil began to boil after about 1½ hours and the heating continued for about 3 hours. The dibromide in ether was washed successively with dilute sodium bicarbonate solution and water, dried and fractionated, b. p. 145-48°/55-60 mm. It is a colourless mobile oil, yield 50 g. (Found : Br, 61·52. $C_7H_{14}Br_2$ requires Br, 62·01 per cent).

3-*Methylsuberonitrile.*—1:6-Dibromo-3-methylhexane (13 g.) was heated with finely powdered potassium cyanide (7·4 g.) in alcohol (75 c.c.) for 12 hours on a steam-bath After removing the alcohol under reduced pressure, the residual oil was taken up in ether and the precipitated potassium bromide was thoroughly extracted with ether, the solvent was removed and the remaining oil was fractionated. A very small amount boiling at 124-26°/55 mm. was identified to be the unchanged dibromide and the second fraction, a colourless mobile liquid, b. p. 160-164°/20 mm., was the dicyanide. This was purified by repeated fractionation, yield 3 g. (Found : C, 71·8 ; H, 9·1. $C_9H_{14}N_2$ requires C, 72·0 ; H, 9·3 per cent). It had d_4^{32}, 0·9506 ; n_D^{32}, 1·44886 ; whence $[R_L]_D$, 42·67 (calc. 43).

3- *Methylsuberic Acid.*—3-Methylsuberonitrile (15 g.) was hydrolysed by boiling with six times its volume of concentrated hydrochloric acid for 8 hours. The thick oily mass floating on the surface was taken up in ether and the ethereal solution was extracted with sodium carbonate solution. The alkali-washings together with the neutralised mother-liquor were evaporated to dryness and the acid isolated by ether after acidification as a thick oil which solidified slowly on keeping in an evacuated desiccator. After crystallisation from dry ether it had m.p 146°. [Found : C, 57·1 ; H, 8·6. M. W. (titration), 187·5. $C_9H_{16}O_4$ requires C, 57·4 ; H, 8·5 per cent. M. W , 188).

4-*Methylcycloheptanone.*—Methylsuberic acid (15 g.) was converted into calcium salt *via* its ammonium salt with slaked lime (12 g.). The solution was evaporated to dryness on a water-bath and the dry mass was then intimately mixed with iron-filings (10 g.). The mixture was distilled in an atmosphere of dry nitrogen. At first the temperature was kept low when mainly water distilled over. The temperature was then gradually raised to 300-350° when a mobile brownish liquid distilled over very slowly, the operation taking about 6 hours. The oil possessed the strong odour of peppermint and gave a semicarbazone in methyl alcoholic solution.

The oily layer of the distillate was taken up in ether and the ethereal solution was dried over anhydrous magnesium sulphate. The *cyclo*heptanone recovered from ether was distilled at 105-10°/45-50 mm. and was identified by the semicarbazone, m.p. 158-59° after several crystallisations. It did not depress the m.p. of the semicarbazone previously described.

Dry *p*-methyl*cyclo*hexanone (14 g.), purified through its bisulphite compound, was added to a solution of diazomethane (7 g.) in dry ether (450 c.c.) cooled in ice. No significant evolution of nitrogen took place even on standing for some time at 0°, but on the addition of 100 c.c. of methyl

alcohol, a vigorous evolution of nitrogen began. After two hours the reaction was almost complete and the mixture was allowed to stand at the room temperature. The nearly colourless solution became colourless after 2 days. The solution was then freed from a slight flocculent precipitate, ether was removed and the mixture of ketones was converted into semi-carbazones, which melted at 140-45°. The non-ketonic product was taken up in ether. After-repeated crystallisations from methyl alcohol the semicarbazone had m.p. 157-59° and did not depress the m.p. of the semicarbazone of methyl*cyclo*heptanone described previously. The yield of the ketone by this method appears to be fairly satisfactory.

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C-ALKYLRESORCINOLS. PART IV. NUCLEAR METHYLATION OF 4-ACYLRESORCINOLS.

By H. A SHAH AND R. C. SHAH.

The nuclear methylation of various 4-acyl-resorcinols, *viz.*, respropiophenone, resbutyrophenone, 2·4-dihydroxyphenylbenzyl ketone and 2·4-dihydroxybenzophenone has been studied.

Respropiophenone on nuclear methylation affords 2-hydroxy-3-methyl-4 methoxy-propiophenone, demethylation of which affords 2 4-dihydroxy-3-methylpropiophenone which is identical with the ketone prepared by the application of the Hoesch reaction to 2-methylresorcinol and propionitrile. Kostanecki acetylation of the nuclear methylated ketone affords 7-methoxy 2 :3 .8-trimethylchromone. Similarly the nuclear methylation of the other 4-acylresorcinols has been studied

In connection with our work on "γ-substitution in the resorcinol nucleus" (Shah and Shah, *J. Chem. Soc.,* 1939, 132, 300, 949) it was found necessary to synthesise 2-methyl-4-alkylresorcinols by an unambiguous method. It was thought of interest to investigate the nuclear methylation of various 4-acylresorcinols, *viz.*, respropiophenone, resbutyrophenone, 2:4-dihydroxyphenylbenzyl ketone and 2:4-dihydroxybenzophenone.

Respropiophenone on nuclear methylation by the method of Robinson and Shah (*J. Chem. Soc.,* 1934, 1491) affords a ketone whose constitution as 2-hydroxy-3-methyl-4-methoxypropiophenone (I, R=C_2H_5) has been established as follows : (*i*) The ketone (I, R = C_2H_5) on demethylation affords 2:4-dihydroxy-3-methylpropiophenone, identical with the compound obtained by the Hoesch reaction on 2-methylresorcinol and propionitrile. Kostanecki acetylation of the ketone (I, R=C_2H_5) with sodium acetate and acetic anhydride affords 7-methoxy-2:3.8-trimethylchromone (II, R'=CH_3), whose constitution is established by its hydrolysis with alkali to 2-hydroxy-3-methyl-4-methoxypropiophenone and 2 hydroxy-3-methyl-4-methoxybenzoic acid (Shah and Laiwalla, *J. Chem. Soc.,* 1938, 1828, Perkin, *ibid.,* 1895, 67, 993).

(I)

(I) →OMe ... Me O ... C·Me ... C·R' ... CO (II)   NaOH →   OMe ... Me ... OH ... COOH   where R = C_2H_5, C_3H_7 or $CH_2·Ph$ R' = R $minus$ CH_2.

Resbutyrophenone similarly affords 2-hydroxy-3-methyl-4-methoxy-butyrophenone (I, R = C_3H_7), demethylation of which gives 2:4-dihydroxy-3-methylbutyrophenone, identical with the ketone prepared from 2-methyl-resorcinol and butyronitrile. Kostanecki acetylation of the ketone (I, R = C_3H_7) with sodium acetate and acetic anhydride affords 7-methoxy-2:8-dimethyl-3-ethylchromone (II, R = C_2H_5) whose constitution has been established by its alkaline hydrolysis to 2-hydroxy-3-methyl-4-methoxybutyro-phenone and 2-hydroxy-3-methyl-4-methoxybenzoic acid.

2:4-Dihydroxyphenylbenzyl ketone similarly affords 2-hydroxy-3-methyl-4-methoxyphenylbenzyl ketone (I, R = CH_2Ph), demethylation of which gives 2:4-dihydroxy-3-methylphenylbenzyl ketone, identical with the ketone prepared from 2-methylresorcinol and benzyl cyanide. The ketone (I, R = CH_2Ph) on Kostanecki acetylation gives 7-methoxy-2:8-dimethyl-isoflavone (II, R' = Ph).

Kostanecki and Tambor (*Ber.*, 1895, **28**, 2305) obtained by the nuclear methylation of 2:4-dihydroxybenzophenone 2:4-dihydroxy-3-methylbenzo-phenone and 2-hydroxy-3-methyl-4-methoxybenzophenone. The same subs-tances were prepared by Jones and Robertson (*J. Chem. Soc.*, 1932, 1689) by the Hoesch reaction of 2-methylresorcinol and benzonitrile and subse-quent methylation of the ketone obtained. Kostanecki and Tambor (*loc. cit.*), however, have given no experimental details. We have isolated on nuclear methylation of 2:4-dihydroxybenzophenone only 2-hydroxy-3-methyl-4-me-thoxybenzophenone, demethylation of which affords 2:4-dihydroxy-3-methyl-benzophenone, identical with the compound prepared by Jones and Robertson. Acetylation of 2-hydroxy-3-methyl-4-methoxybenzophenone affords 7-me-thoxy-4-phenyl-8-methylcoumarin.

E X P E R I M E N T A L.

2-Hydroxy-3-methyl-4- methoxypropiophenone (I, R = C_2H_5).— Potassi-um hydroxide (27·5 g., 4 mols.) was dissolved in methanol (110 c. c.) and respropiophenone (20 g.) was added. The mixture was cooled in a freezing mixture and methyl iodide (85·5 g., 5 mols.) was added all at once with shaking. If two layers separated homogeneity was restored by the

addition of more methyl alcohol. The temperature was then gradually allowed to rise, when potassium iodide separated. Next day the mixture was refluxed for 6 hours. The methanol was removed and the dark solid residue was acidified and filtered. It was then macerated with sodium hydroxide solution (200 c.c., 5%). The insoluble 2-hydroxy-4-methoxy-3-methyl-propiophenone crystallised from alcohol in colourless slender pointed needles (5·2 g.), m. p. 78-79°. (Found: C, 68·1; H, 7·2. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·4 per cent). It is insoluble in alkali and gives a reddish brown colouration with alcoholic ferric chloride.

Demethylation of 2-Hydroxy-4-methoxy-3-methylpropiophenone.—(i) A mixture of 2-hydroxy-4-methoxy-3- methylpropiophenone (1 g.) and aluminium chloride (2 g.) was heated at 135-40° for 3 hours, ice and hydrochloric acid were added and the insoluble solid collected. It was treated with sodium hydroxide solution (50 c.c., 5%) and filtered. The alkaline solution on acidification gave the ketone, 2:4-dihydroxy-3-methyl-propiophenone, which crystallised from water in rosy needles, m. p. 128-30°. It did not depress the m. p. when mixed with a sample of 2:4-hydroxy-3-methylpropiophenone prepared by the application of the Hoesch reaction to 2-methylresorcinol and propionitrile.

(ii) 2-Hydroxy-4-methoxy-3-methylpropiophenone (1 g.) was dissolved in acetic anhydride (10 c.c.) and hydriodic acid (d 1·7, 20 c.c.) added drop by drop. The reaction mixture was refluxed at 130-40° for 2 hours. It was poured into a saturated solution of sodium bisulphite (200 c.c.) and the yellow solid which separated out was crystallised from water, m.p. 128-29°, yield 0·6 g.

7-Methoxy-2 : 3 : 8-trimethylchromone (II, R′=CH₃).—A mixture of 2-hydroxy-3-methyl-4-methoxypropiophenone (1 g.), sodium acetate (3 g.) and acetic anhydride (20 c.c.) was heated at 175-85° for 8 hours. The reaction mixture was poured into water (500 c.c.). The chromone crystallised from dilute alcohol in colourless slender needles, m.p. 69-70°, yield 0·5 g. (Found. C, 66·2; H, 6·7. $C_{13}H_{14}O_3$, H_2O requires C, 66·1, H, 6·8 per cent).

Hydrolysis of 7-Methoxy-2 : 3 : 8-trimethylchromone.—A mixture of the chromone (0·5 g.) and sodium hydroxide solution (30 c.c., 5 %) was refluxed on a sand-bath for 3 hours. On cooling a substance separated out as colourless, wooly needles, which were identified as 2-hydroxy-3-methyl-4-methoxypropiophenone by direct comparison. The alkaline solution was acidified and the precipitated acid purified by treatment with sodium bicarbonate. The acid was identified as 2-hydroxy-3-methyl-4-methoxy-benzoic acid (Perkin, *loc. cit.*) by direct comparison.

2-Hydroxy-3-methyl-4-methoxybutyrophenone (I, R = C_3H_7).—A solution of resbutyrophenone (22 g.) in methyl alcoholic potash (28 g. of caustic potash in 112 c.c. of methanol) was cooled to 0° and methyl iodide (88 g.) added all at once with shaking. Next day the reaction mixture was refluxed for 6 hours, filtered from the insoluble potassium iodide and kept in a frigidaire for 2 days. The yellow crystalline solid that separated out was washed with sodium hydroxide solution (100 c.c., 5%). It crystallised from alcohol in colourless rectangular plates, m.p. 82-84°, yield 6 g. (Found : C, 69·0 ; H, 7·8. $C_{12}H_{16}O_3$ requires C, 69·7 ; H, 8·2 per cent).

2 : 4-*Dihydroxy-3-methylbutyrophenone.*—A mixture of the ketone (1 g.), acetic anhydride (10 c.c.) and hydriodic acid (20. c. c.) was refluxed at 125-35° for 2 hours. The reaction mixture was poured into a saturated solution of sodium bisulphite (200 c.c.). The solution was extracted with ether, the extract washed with aqueous sodium hydroxide (50 c.c., 5%). The alkaline solution on acidification gave 2 : 4-dihydroxy-3-methylbutyrophenone which crystallised from water as straw-coloured needles, m.p. 155-57°, yield 0·4 g. It did not depress the m.p. of a sample prepared by the application of the Hoesch reaction to 2-methylresorcinol and butyronitrile.

7-*Methoxy*-2 : 8-*dimethyl-3-ethylchromone* (II, R' = C_2H_5).—A mixture of 2-hydroxy-3-methyl-4-methoxybutyrophenone (2 g.), sodium acetate (5 g.) and acetic anhydride (30 c.c.) was refluxed at 180-85° for 8 hours. The reaction mixture was poured into water (300 c.c.) and the brownish red oil, which separated, was washed with sodium bicarbonate. It distilled at 173°/6 mm. as a yellow oil which solidified on cooling. It crystallised from alcohol in colourless rectangular prisms, m.p. 43-45°. (Found : C, 67·4; H, 7·4. $C_{14}H_{16}O_3$, H_2O requires C, 67·2, H, 7·2 per cent).

Hydrolysis of 7-*Methoxy*-2 : 8-*dimethyl-3-ethylchromone.*—The hydrolysis was carried out as in the case of 7-methoxy-2 : 3 : 8-trimethylchromone. The products, 2-hydroxy-3-methyl-4-methoxybutyrophenone and 2:4-dimethoxy-3-methylbenzoic acid, were identified.

2-Hydroxy-3-methyl-4-methoxyphenylbenzyl Ketone (I, R = CH₂PH).—A solution of 2:4-dihydroxyphenylbenzyl ketone (20 g.) in methyl alcoholic potash (from 20 g. of caustic potash and 80 c.c. of methanol) was cooled to 0° and methyl iodide (62 g.) was added all at once with shaking. Next day the reaction mixture was refluxed for 6 hours. Methanol was removed and the dark brown solid was macerated with sodium hydroxide solution (200 c.c., 4%). The insoluble 2-hydroxy-3-methyl-4-methoxyphenylbenzyl ketone crystallised from alcohol in colourless prisms, m.p. 110-11°, yield 10 g. (Found : C, 75·1 ; H, 6·3. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3 per cent).

2 : 4-*Dihydroxy-3-methylphenylbenzyl Ketone*.—A mixture of the above-mentioned ketone (3 g.), acetic anhydride (20 c.c.) and hydriodic acid (30 c.c.) was refluxed at 125-35° for 2 hours. The reaction mixture was poured into a saturated solution of sodium bisulphite (200 c.c.) and the yellow solid was crystallised from benzene (charcoal) as colourless needles, m.p. 157-59°, yield 1·8 g. The m.p., after admixture with a specimen prepared by the application of Hoesch reaction to 2-methylresorcinol and benzyl cyanide, was not depressed.

7-*Methoxy-2* : 8-dimethyl*isoflavone* (II, R′=Ph).—A mixture of 2-hydroxy-3- methyl- 4-methoxyphenylbenzyl ketone (3 g.), sodium acetate (6 g.) and acetic anhydride (30 c.c.) was refluxed at 175-85° for 8 hours. The reaction mixture was poured into water (300 c.c.). The *iso*flavone crystallised from dilute methanol in colourless needles, m.p. 140-42°, yield 1·5 g. (Found : C, 77·0 ; H, 5·6. $C_{18}H_{16}O_3$ requires C, 77·1 ; H, 5·7 per cent).

2-*Hydroxy-3-methyl-4-methoxybenzophenone*.—A solution of 2 : 4-di-hydroxybenzophenone (20 g.) in methyl alcoholic potash (21 g. of caustic potash in 84 c.c. of methanol) was cooled to 0° and methyl iodide (66 g.) was added. The product was isolated in the usual manner. 2-Hydroxy-4-methoxy-3-methylbenzophenone crystallised from alcohol in yellow rectangular prisms, m.p. 125°, yield 6 g. Jones and Robertson (*loc. cit.*) give m.p. 125°.

2 : 4-*Dihydroxy-3-methylbenzophenone*.—A mixture of the preceding ketone (1 g.), acetic anhydride (10 c.c.) and hydriodic acid (15 c.c.) was refluxed at 125-35° for 2 hours. The mixture was poured into a saturated solution of sodium bisulphite (200 c.c.) and the reddish yellow solid was crystallised from dilute alcohol, m.p. 177°, yield 0·6 g. Jones and Robertson (*loc. cit.*) give m.p. 177°.

7-*Methoxy-4-phenyl-8-methylcoumarin*.—A mixture of 2-hydroxy-3-methyl-4-methoxybenzophenone (1 g.), sodium acetate (2 g.) and acetic anhydride (20 c.c.) was refluxed at 180-90° for 1 hour. The reaction mixture was poured into water (300 c.c.). The coumarin crystallised from dilute alcohol in colourless slender needles which changed into prisms, m.p. 94-95°, yield 0·5 g. (Found : C, 71·9 ; H, 5·7. $C_{17}H_{14}O_3$, H_2O requires C, 71·8 ; H, 5·6 per cent).

PECHMANN CONDENSATION OF METHYL β-RESORCYLATE WITH SOME β-KETONIC ESTERS.

By S. M. SETHNA AND R. C. SHAH.

Methyl β-resorcylate has been condensed with ethyl α-chloro and- α-benzoyl aceto acetates and with ethyl acetone dicarboxylate in the presence of sulphuric acid. The results obtained show that as in the condensation of methyl β-resorcylate with ethyl α-alkyl-acetoacetates, the 4-carbomethoxy group in the resorcinol nucleus has only little retarding influence on the Pechmann condensation.

In continuation of the previous work (*J. Indian Chem. Soc.*, 1937, 1**4**, 717; 1938, 1**5**, 383) methyl β-resorcylate has been condensed with ethyl α-chloro- and ethyl α-benzoylacetoacetates and with ethyl acetone dicarboxylate. The products obtained have been found to be methyl 7-hydroxy-3-chloro-4-methylcoumarin-6-carboxylate (I, R = Me), methyl 7-hydroxy-4-phenylcoumarin-6-carboxylate (II, R = Me) and ethyl 7-hydroxy-6-carbomethoxycoumarin-4-acetate (III, R = Me, R′ = Et).

In the case of ethyl α-benzoylacetoacetate the acetyl group is split off in the course of the reaction as observed by Pechmann and Hanke (*Ber.*, 1901, 3**4**, 356).

The constitution of the coumarin esters (I and II, R = Me) has been proved by hydrolysis to the corresponding acids (I and II, R = H) and subsequent decarboxylation of the acids. The decarboxylated products have been proved to be identical with authentic specimens of 7-hydroxy-3-chloro-4-methylcoumarin and 7-hydroxy-4-phenylcoumarin, prepared from resorcinol and ethyl α-chloro- and ethyl α-benzoylacetoacetate.

On hydrolysis, the coumarin ester (III, R = Me; R′ = Et) gives the known 7-hydroxy-4-methylcoumarin-6-carboxylic acid (Shah *et al.*, *J. Indian Chem. Soc.*, 1937, 1**4**, 717) instead of 7-hydroxy-6-carboxycoumarin-4-acetic acid (III, R = H.; R′ = H).

The results obtained show in agreement with our previous work (*loc. cit.*) on the condensation of methyl β-resorcylate with ethyl α-alkyl-acetoacetates that the 4-carbomethoxy group in the resorcinol nucleus has only little retarding influence on the Pechmann condensation.

E x p e r i m e n t a l.

Methyl 7-Hydroxy-3-chloro-4-methylcoumarin-6-carboxylate (I, R=Me).
—To a mixture of methyl β-resorcylate (5 g.) and freshly distilled ethyl
α-chloroacetoacetate (5 g.) sulphuric acid (80%, 45 c c.) was added with
shaking. After keeping the reaction mixture for 20 hours it was added to
cold water. The product was washed with sodium bicarbonate solution
and crystallised from rectified spirit in colourless glistening needles
(0·5 g.), m.p. 218-20°. (Found : C, 53·7 ; H, 3·4. $C_{12}H_9O_5Cl$ requires
C, 53·6; H, 3·4 per cent).

The *acetyl derivative*, prepared as usual by refluxing the ester with
acetic anhydride and pyridine, was crystallised from rectified spirit in
needles, m.p. 169-70°. (Found : C, 54·2 ; H, 3·6. $C_{14}H_{11}O_6Cl$ requires
C, 54·1; H, 3·5 per cent).

The *methyl ether*, prepared by refluxing the acetone solution of the
ester (0·2 g.) with fused potassium carbonate (0·5 g.) and methyl iodide
(3 c.c.) for 20 hours, was crystallised from rectified spirit in needles,
m.p. 218-19°. (Found : C, 55·3; H, 3·8. $C_{13}H_{11}O_5Cl$ requires C, 55·2 ;
H, 3·9 per cent).

7-Hydroxy-3-chloro-4-methylcoumarin-6-carboxylic Acid (I, R=H).—
The ester (0·5 g.) was shaken up with sodium hydroxide (10%, 15 c.c.)
and kept overnight. The next day the solution was acidified with hydro-
chloric acid and the acid crystallised from rectified spirit in shining
needles, m.p. 265-67° (efferv.). (Found : C, 48·8 ; H, 3·3. $C_{11}H_7O_5Cl$,
H_2O requires C, 48·4 ; H, 3·3 per cent).

The acid (0·1 g.) was decarboxylated by heating in a sealed tube with
water (15 c.c.) for 9 hours at 180-90°. The product crystallised
from dilute alcohol in needles, m.p. 240°. Mixed m.p. with an authentic
specimen of 7-hydroxy-3-chloro-4-methylcoumarin, obtained from resorcinol
and ethyl α-chloroacetoacetate, was not depressed. Pechmann and Hanke
(*loc. cit.*) give m.p. 236°.

Methyl 7-hydroxy-4-phenylcoumarin-6-carboxylate (II, R=Me).—To a
mixture of methyl β-resorcylate (5 g.) and ethyl α-benzoylacetoacetate (6 g.)
sulphuric acid (80%, 25 c.c.) was added gradually with shaking. After
keeping for 45 hours the reaction mixture was added to cold water. The
oily mass which separated partially solidified on keeping in a frigidaire for
2 days. It was filtered, treated with sodium bicarbonate solution and the
insoluble portion crystallised from rectified spirit in pale green needles
(0·5 g.), m.p. 200-1°. (Found : C, 68·6; H, 4·0. $C_{17}H_{12}O_5$ requires
C, 68·9 ; H, 4·1 per cent).

The *acetyl derivative* crystallised from rectified spirit in needles, m.p. 160-61°. (Found : C, 67·6; H, 4·2. $C_{19}H_{14}O_6$ requires C, 67·5; H, 4·1 per cent).

7-Hydroxy-4-phenylcoumarin-6-carboxylic Acid (II, R=H).—The sodium bicarbonate solution from above was acidified with hydrochloric acid and the product crystallised from rectified spirit in pale green tiny needles (0·2 g.), m.p. 285°. (Found : C, 67·7; H, 3·7. $C_{16}H_{10}O_5$ requires C, 68·1 ; H, 3·5 per cent). The acid can also be obtained by keeping the ester with 10% sodium hydroxide solution for about 60 hours.

The acid was decarboxylated by heating in a sealed tube with water as usual. The product was treated with sodium bicarbonate solution to remove undecarboxylated acid. The insoluble portion crystallised from rectified spirit in thin plates, m.p. 242-44°. Mixed m.p. with an authentic specimen of 7-hydroxy-4-phenylcoumarin was not depressed. Pechmann and Hanke (*loc. cit.*) give m.p. 243-44°.

Ethyl 7-hydroxy-6-carbomethoxycoumarin-4-acetate (III, R=Me ; R'=Et).—To a mixture of methyl β-resorcylate (5 g.) and ethyl acetone dicarboxylate (6·1 g.), sulphuric acid (80%, 45 c.c.) was added with stirring and after keeping for 20 hours the reaction mixture was added to cold water. The product was treated with sodium bicarbonate solution. The insoluble portion crystallised from rectified spirit in glistening needles (0·7 g.), m.p. 194-96°. (Found : C, 58·2 ; H, 4·4. $C_{15}H_{14}O_7$ requires C, 58·9; H, 4·6 per cent).

The *acetyl derivative* was crystallised from dilute alcohol in needles, m.p. 148-49°. (Found : C, 58·5; H, 4·3. $C_{17}H_{16}O_8$ requires C, 58·6; H, 4·6 per cent).

7-Hydroxy-6-carbomethoxycoumarin-4-acetic Acid (III, R=Me ; R'=H). —The sodium bicarbonate solution from above was acidified with hydrochloric acid and the product obtained was crystallised from rectified spirit in clusters of tiny needles (1 g.), m.p. 184-86° (efferv.). (Found : C, 56·3; H, 3·6. $C_{13}H_{10}O_7$ requires C, 56·1; H, 3·6 per cent).

The acid on decarboxylation by heating to its melting point till the effervescence ceased gave methyl 7-hydroxy-4-methylcoumarin-6-carboxylate (Shah *et al.*, *loc. cit.*), m.p. and mixed m.p. 212-14°.

Hydrolysis of Ethyl 7-Hydroxy-6-carbomethoxycoumarin-4-acetate.—The ester (0·1 g.) was heated in a boiling water-bath for 25 minutes with sodium hydroxide (5%, 10 c.c.) and the solution was acidified. The product was crystallised from rectified spirit in tiny needles, m.p. 285°, mixed m.p. with 7-hydroxy-4-methylcoumarin-6-carboxylic acid (Shah *et al.*, *loc. cit.*) was not depressed.

Attempts were made to hydrolyse the ester by keeping in contact with cold sodium hydroxide for 30-40 hours, but the desired acid 7-hydroxy-6-carboxycoumarin-4-acetic acid could not be obtained, 7-hydroxy-4-methyl-coumarin-6-carboxylic acid being formed.

All the analyses recorded are micro-analyses.

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FURANO COMPOUNDS. PART I. SYNTHESIS OF FURO-3'-METHYL-5:6 (4':5')-COUMARIN AND FURO-3'-ETHYL-5:6 (4':5')-COUMARIN.

By H. A. SHAH AND R. C. SHAH.

Ethyl 5-hydroxy-6-acetylcoumarin-3-carboxylate on condensation with ethyl bromoacetate affords ethyl 3-carbethoxy-6-acetylcoumarin-5 -O- acetic ester, which on subsequent hydrolysis and ring-closure affords furo-3'-methyl-5:6 (4':5")-coumarin-3-carboxylic acid. The foregoing acid on decarboxylation affords furo-3'-methyl-5:6 (4':5")-coumarin. Similarly furo-3'-ethyl-5:6 (4':5')-coumarin was synthesised starting from ethyl 5-hydroxy-6-propionylcoumarin-3-carboxylate.

Furocoumarins, derived from 5-hydroxycoumarin, are not known with the exception of 3:4'-dimethyl-5':6'-furocoumarin synthesised by Kelkar and Ranade (*Rasayanam*, 1938, **1**, 151) by condensation of 5-hydroxy-6-acetyl-4-methylcoumarin (Sethna, Shah and Shah, *J. Chem. Soc.*, 1938, 228) with ethyl bromoacetate, subsequent hydrolysis and ring-closure. However, furocoumarins, unsubstituted in the 4-position, cannot be obviously prepared by this method.

As a part of the comprehensive investigation of the synthetical possibilities of 2:4-dihydroxy-3-formylacetophenone (Shah and Shah, *J. Chem. Soc.*, 1939, 132 and subsequent papers) and other ketone-aldehydes, we have synthesised furo-3'-methyl-5:6-(4':5')-coumarin and furo-3'-ethyl-5:6(4':5')-coumarin.

Ethyl 5-hydroxy-6-acetylcoumarin-3-carboxylate (I, R = Me ; R' = Et) (Shah and Shah, *loc. cit.*), now prepared by the esterification of 5-hydroxy-6-acetylcoumarin-3 carboxylic acid, on condensation with ethyl bromoacetate in acetone solution in presence of potassium carbonate affords ethyl 3-carbethoxy-6-acetylcoumarin-5-O-acetic ester (II, R = Me ; R' = Et). On hydrolysis with dilute alkali (II) gives 3-carboxy-6-acetylcoumarin-5-O-acetic acid (II, R = Me ; R' = H), which on treatment with sodium acetate and acetic anhydride affords furo-3'-methyl-5:6(4':5')-coumarin-3-carboxylic acid (III, R = Me; R' = H). On decarboxylation with quinoline and copper

(I)   (II)

6·

(III)

(IV)

bronze (III) gives furo-3'-methyl-5:6 (4':5')-coumarin (IV, R = Me). The synthesis of the furocoumarin incidentally establishes the structure assigned to ethyl 5-hydroxy-6-acetylcoumarin-3-carboxylate on account of its positive ferric chloride reaction (Shah and Shah, *loc. cit.*).

Similarly from ethyl 5-hydroxy-6-propionylcoumarin-3-carboxylate (I, R = Et ; R' = Et) furo-3'-ethyl-5:6(4':5')-coumarin (IV, R = Et) has been synthesised through the stages: ethyl 3-carbethoxy-6-propionylcoumarin-5-*O*-acetic ester (II, R = R' = Et), 3-carboxyl-6-propionylcoumarin-5-*O*-acetic acid (II, R = Et ; R' = H), furo-3'-ethyl-5:6 (4':5')-coumarin-3-carboxylic acid (III, R = Et; R' = H).

EXPERIMENTAL.

Ethyl 5-Hydroxy-6-acetylcoumarin-3-carboxylate (I, R = Me ; R' = Et).— A mixture of 5-hydroxy-6-acetylcoumarin-3-carboxylic acid (Shah and Shah, *loc. cit.*) (13 g.), ethyl alcohol (260 c.c.) and concentrated sulphuric acid (15 c.c.) was heated under reflux for 18 hours. The reaction mixture was cooled and the straw-coloured solid separating was filtered and washed with aqueous sodium bicarbonate to remove the unchanged acid. The product crystallised from alcohol in straw-coloured plates (12 g.), m. p. 155-56°. Shah and Shah (*loc. cit.*) gave m. p. 155-56°.

Ethyl 3-Carbethoxy-6-acetylcoumarin-5-O-acetic Ester (II, R = Me ; R' = Et).—The coumarin ester (5 g.), ethyl bromoacetate (5 g.) and fused potassium carbonate (5 g.) in acetone (300 c.c.) were heated under reflux for 18 hours, the solution filtered and the residue washed thoroughly with acetone (50 c.c.). Acetone and excess of ethyl bromoacetate were removed in a current of air and the solid obtained crystallised from alcohol as pale yellow clusters of needles, m.p. 113-15°. (Found: C, 59·7 ; H, 5·0. $C_{18}H_{18}O_8$ requires C, 59·7; H, 5·0 per cent).

3-Carboxyl-6-acetylcoumarin-5-O-acetic Acid (II, R = Me ; R' = H).— A suspension of the preceding compound (1 g.) was hydrolysed in 4% sodium hydroxide solution (20 c.c.) by heating on the steam-bath for 30 minutes. 3-Carboxy-6-acetylcoumarin-5-*O*-acetic acid, isolated by acidifi-

cation, was crystallised from hot water in colourless wooly needles (o·6 g.), m.p. 189-91° (decomp.). (Found: C, ·55·2 ; H, 3·3. $C_{14}H_{10}O_8$ requires C, 54·9; H, 3·3 per cent). It is easily soluble in alcohol and hot water.

Furo -3'-methyl-5:6(4':5')-coumarin-3-carboxylic Acid (III, R = Me ; R'=H).—A mixture of the foregoing acid (o·5 g.), fused sodium acetate (5 g.) and acetic anhydride (20 c.c.) was heated under reflux for 2 hours. The reaction mixture was poured into water (200 c.c.) and the precipitated pale yellow solid collected and crystallised first from dilute alcohol and then from water in tiny shining pale yellow needles (o·3 g.), m.p. 226-28° (decomp.). (Found: C, 63·6 ; H, ·3·4. $C_{13}H_8O_5$ requires C, 63·9 ; H ; 3·3 per cent). It is easily soluble in alcohol and sparingly in water.

3'-Methyl-5:6(4':5')-furocoumarin (IV, R = Me).—The foregoing acid (o·2 g.) was boiled with quinoline (10 c.c.) containing copper bronze (o·5 g.) for 45 minutes. The filtered solution was mixed with an excess of dilute hydrochloric acid and extracted with ether, the extract washed with aqueous sodium bicarbonate and evaporated. The residual furo-3'-methyl-5 :6(4':5')-coumarin was crystallised from hot water in colourless wooly needles, m.p. 138-40°. (Found : C, 71·7 ; H, 4·2. $C_{12}H_8O_3$ requires C, 72·0 ; H, 4·0 per cent). It is insoluble in cold sodium hydroxide solution.

Ethyl 5-Hydroxy-6-propionylcoumarin-3-carboxylate (I, R = Et ; R'=Et). —A mixture of 5-hydroxy-6-propionylcoumarin -3-carboxylic acid (6 g.), ethyl alcohol (100 c.c.) and concentrated sulphuric acid (6 c.c.) was heated under reflux for 18 hours and the ester isolated as before and crystallised from alcohol in straw-coloured slender pointed needles, m. p. 152-54°. (Found: C, 62·0; H, 5·0. $C_{15}H_{14}O_6$ requires C, 62·1 ; H, 4·8 per cent).

Ethyl 3-Carbethoxy -6 -propionylcoumarin-5-O-acetic Ester (R = Et; R'=Et).—The coumarin ester (5 g.), ethyl bromoacetate (5 c.c.) and potassium carbonate (5 g.) in acetone (200 c.c.) was heated under reflux for 18 hours, the solution filtered and the residue washed thoroughly with acetone (50 c.c.). Acetone and excess of ethyl bromoacetate were removed in a current of air and the solid obtained crystallised from alcohol as colourless clusters of needles (2 g.), m. p. 103-5°. (Found: C, 60·7 ; H, 5·4. $C_{19}H_{20}O_8$ requires C, 60·6; H, 5·3 per cent).

3-Carboxyl-6-propionylcoumarin 5-O-acetic Acid (II, R = Et ; R'=H).— A suspension of the preceding compound (1 g.) in 4% sodium hydroxide solution (20 c.c.) was heated on the steam-bath for 30 minutes. The acid, isolated with dilute hydrochloric acid, was crystallised from hot water in colourless needles (o·5 g.), m.p. 194-96°. (Found: C, 56·3 ; H, 3·8. $C_{15}H_{12}O_8$ requires C, 56·3 ; H, 3·8 per cent).

Furo - 3'-ethyl-5:6 (4':5')-coumarin-3-carboxylic Acid (III, R=Et; R'=H).—A mixture of the foregoing acid (0·5 g.), fused sodium acetate (2·5 g.) and acetic anhydride (20 c.c.) was heated under reflux for 1 hour and the separated yellow solid collected. It crystallised from water containing a few drops of alcohol in shining, slender, yellow needles, m.p. 157-58°. (Found : C, 61·0 ; H, 4·50. $C_{14}H_{10}O_5$, H_2O requires C, 60·9 H, 4·4 per cent).

Furo-3'-ethyl-5:6(4':5')-coumarin (IV, R=Et).—The foregoing acid (0·2 g.) was boiled with quinoline (10 c.c.) containing copper bronze (0·4 g.) for 45 minutes. The filtered solution was mixed with an excess of dilute hydrochloric acid and extracted with ether, the extract washed with aqueous sodium bicarbonate and evaporated. The residual furocoumarin crystallised from hot water in colourless wooly needles, m.p. 150-52°. (Found: C, 72·5; H, 4·9. $C_{13}H_{10}O_3$ requires C, 72·9; H, 4·7 per cent).

NATURAL FLAVONES. PART IV. ON THE CONSTITUTION OF ERIANTHIN, THE YELLOW COLOURING MATTER OF *BLUMEA ERIANTHA* DC.

BY PRAFULLA KUMAR BOSE AND PHANIBHUSAN DUTT.

Erianthin, the yellow colouring matter of *Blumea eriantha* DC., has been shown to be 5 :7-dihydroxy-3 :6 :8 :3' :4'-pentamethoxyflavone.

Blumea eriantha DC (N. O. *Compositae*), a native of Western India, has only a restricted use in Indian medicine. A warm infusion of the plant is given as a sudorific in catarrhal affections. It is also considered to be diuretic and emmenagogue. Dymock, Warden and Hooper (*Pharmacographia Indica*, Vol. II, p. 254) reported the presence of the following constituents in the plant : chlorophyll, a dark acid resin, tannin (trace), a volatile oil, a wax and a crystalline, yellow, nitrogen-free compound, m.p. 155°. The colour reactions and the behaviour of the last compound towards acids and alkali were also recorded by them.

The essential oil of *B. eriantha* has been the subject of a recent investigation (Schimmel's Report, 1937, p. 8 ; cf. also Amin and Patel, *Proc. Indian Science Congress*, 1936, p. 200). It contains 95% ketones, the chief constituent of which is *d*-carvotanacetone.

The present communication deals with the isolation and examination of the colouring matter mentioned above. By the method described in the Experimental we have been able to obtain it in a yield not exceeding 0·03 %. The crude substance melted at 154°, but on careful purification the m.p. rose to 161°. The properties of this compound agreed with those of Dymock's colouring matter. We propose the name ' Erianthin ' for this substance, which appears to be a new natural product. Erianthin forms yellow transparent prisms or needles which dissolve in alcoholic potassium hydroxide, or concentrated hydrochloric acid with a deep yellow colour. It is insoluble in 0·5 % aqueous alkali, liquor ammonia or dilute mineral acids. It dissolves, however, in 5% aqueous alkali, and the alkaline solution is stable to aerial oxidation. Ferric chloride imparts an olive-green colour to an alcoholic solution of erianthin, but ferrous sulphate does not produce any characteristic colour. Treated with magnesium and hydrochloric acid, alcoholic erianthin produces a pink colour. Apparently it behaves like a hydroxyflavone.

The analytical data of erianthin are in agreement with the formula $C_{15}H_3O_2(OMe)_5(OH)_2$ and it is further supported by the formation of a colourless diacetyl derivative. Hydrolytic fission of erianthin by means of alkali produced an acid, m.p. $177.5°$, which was definitely identified as veratric acid. The partial formula of erianthin may, therefore, be represented by (I).

(OH)$_2$
(OMe)$_3$ (I)

OH
(OMe)$_3$ (II)

We have now to allocate positions to the two OH and three OMe groups in the benzopyrone nucleus, which can have a maximum of five substituents. The stability of an alkaline solution of erianthin in air excludes the possibility of existence of a free OH group in position 3. Both the phenolic groups consequently must be present in the benzene nucleus. On the basis of the hypothesis, put forward by Bose and Nath in Part I of this series (*J. Indian Chem. Soc.*, 1938, **15**, 141), that in natural polyhydroxyflavones or their partially methylated products, a free OH group is always to be found in position 5, the formula (I) may further be expanded to (II). Methylation of erianthin by means of diazomethane led to a crystalline yellow monomethyl derivative. Prolonged contact with the reagent failed to give the dimethyl derivative. Monomethylerianthin gave a green ferric test and a colourless acetyl derivative. These observations may be accepted as an additional evidence of the presence of an OH group in position 5, since the OH group in this particular position is known to resist methylation by diazomethane (*cf.* Robinson and Tseng, *J. Chem. Soc.*, 1938, 1004).

(III)   (IV)

The second OH group must occupy the *meta*-position with regard to the first, because erianthin gives negative tests with alkaline o-dinitrobenzene

(Bose, *J. Indian Chem. Soc., Sir P. C. Ray* 70th Birthday Vol., 1933, 65) as also with chloropentammine cobaltichloride (Shibata and Hattori, *Acta Phytochim.*, 1930, 5, 117). The three remaining positions, namely 3, 6 and 8, must consequently be occupied by the three methoxy groups. In other words, erianthin should be regarded as 5:7-dihydroxy-3:6:8:3':4'-penta-methoxyflavone (III), and monomethylerianthin as (IV).

The isolation of a compound of the type (III) from natural sources is of interest because it happens to be the second known natural product of the heptahydroxyflavone series, the first being gardenin from *Gardenia lucida* (Bose and Nath, *loc. cit.*). Incidentally it might be mentioned that erianthin is one of the few known derivatives of pentahydroxybenzene, occurring in nature.

EXPERIMENTAL.

Isolation of Erianthin.—A supply of *Blumea eriantha* DC., in flower, was obtained from the Bombay Presidency through the kindness of Mr. S. N. Bal, M.Sc., Ph.C., Officer-in-Charge, Botanical Survey of India and Mr. L. S. S. Kumar, Economic Botanist to the Government of Bombay, to whom we offer our best thanks. The air-dried plant (1 kg.) was cut into small pieces and percolated with commercial methyl alcohol during 60 hours. The deep green extract was concentrated to about 900 c.c. and treated while still hot with concentrated aqueous lead acetate (15 c.c.). The precipitate was filtered off and the filtrate freed from lead by means of hydrogen sulphide. The filtrate was concentrated to about 200 c.c. in vacuum and allowed to stand in a cold chamber (0°) for 72 hours. Crude erianthin separated out along with much tarry matter, which was removed by washing with cold alcohol. The mother-liquor and washings gave a second crop of crystals on being kept for about a week in the cold.

The crude erianthin melted at 154°. Repeated crystallisations from chloroform-alcohol and acetone gave yellow transparent prisms, m.p. 161°. Further crystallisations did not improve the m.p. Erianthin was obtained in yields varying from 0·02 to 0·03 %. It is insoluble in petroleum ether, sparingly soluble in alcohol, ether and benzene, moderately soluble in acetone and acetic acid and freely soluble in chloroform. (Found in samples dried at 110° in *vacuo* over P_2O_5 : C, 59·4 ; H, 4·94 ; OMe, 38·54. $C_{20}H_{20}O_9$ requires C, 59·41 ; H, 4·95 ; 5 OMe, 38·36 per cent).

Stability of Alkaline Erianthin in Air.—Through a solution of erianthin in 5% potassium hydroxide a rapid current of air was passed for 1·5 hours. The colour of the solution did not change. On acidification with hydro-chloric acid a pale yellow crystalline precipitate was obtained, which melted

at 160·5°· after crystallisation from acetone, and which did not depress the m.p. of pure erianthin.

Diacetylerianthin.—A mixture of erianthin (o·1 g.), acetic anhydride (2 c.c.) and a drop of pyridine was gently boiled for 3 hours. The liquid products from the reaction mixture were removed under reduced pressure and the crystalline residue was taken up with benzene, charcoaled, and filtered. The filtrate on concentration and dilution with petroleum ether gave colourless needles. Twice recrystallised from benzene-petroleum ether, the acetyl derivative melted at 163°. (Found in sample dried at 110° in *vacuo* over P_2O_5 : OMe, 32·00. $C_{24}H_{24}O_{11}$ requires 5 OMe, 31·8 per cent). It gave no ferric test in alcohol.

Hydrolysis of Erianthin.—Erianthin (o·4 g.) was heated under reflux for 12 hours with alcoholic potassium hydroxide (15 c.c. of 20%). The product was evaporated to dryness, the residue taken up with water and extracted with ether. The ether extract gave a small quantity of red tarry matter, which could not be crystallised. The aqueous portion, on concentration and acidification with hydrochloric acid, gave a crystalline precipitate. This was collected, washed with cold water and purified by sublimation in high vacuum and by subsequent crystallisation from dilute methyl alcohol. The colourless prisms melted at 177·5° and did not depress the m.p. of an authentic specimen of veratric acid, m.p. 177·5-78°. (Found in sample dried at 110° in *vacuo* over P_2O_5 : OMe, 33·3. Calc. for $C_9H_{10}O_4$: 2 OMe, 34·06 percent).

Monmethylerianthin (IV).—Erianthin (o·2 g), dissolved in pure methyl alcohol, was treated with an excess of ethereal diazomethane and the mixture left overnight at room temperature. The residue left after removal of the solvents was distilled at 210-30°/o·02 mm., the yellow distillate was twice crystallised from dilute methyl alcohol as pale yellow needles, m.p. 141°. (Found in sample dried at 100° in *vacuo* over P_2O_5 : OMe, 44·6. $C_{21}H_{22}O_9$ requires 6 OMe, 44·5 per cent). It gave a green colour with ferric chloride in alcohol.

Monomethylmonoacetylerianthin.—The foregoing compound (o·08 g.) was acetylated and the product purified in the manner indicated under diacetylerianthin. The acetyl derivative formed colourless needles, m.p. 131°. It showed no ferric test in alcohol. (Found in sample dried at 100° in *vacuo* over P_2O_5 : OMe, 40·8. $C_{23}H_{24}O_{10}$ requires 6 OMe, 40·42 per cent).

Our best thanks are due to Mr. N. Ghosh, M.Sc., who carried out the micro-analyses recorded in this paper.

INVESTIGATION OF THE OIL FROM THE FRUITS OF FERULA ALLIACEA, BOISS.

BY PRAFULLA KUMAR BOSE AND SACHINDRA NATH DUTT.

The fruits of *F. alliacea* contain 19 per cent of oil and some natural coumarins. The constants of the oil have been determined and its probable composition has been discussed.

Following a scheme for the systematic investigation of plant materials of the *Umbelliferae* order, we took up the present investigation. Although some work on the resin of *F. alliacea* roots have been recorded (Hirschsohn, *Arch. Pharm.*, 1878, **213**, 309 ; Tschrich, *Harze,* 2nd Ed., Vol. I, p. 362), the fruits of this plant do not appear to have been investigated before.

The mature fruits emit a powerful aromatic smell when crushed, apparently due to the presence of a volatile oil. In fact, steam distillation of a petroleum ether extract of the material gave about 0·9% of a colourless oil having a strong sweet smell. The nature of the oil is being investigated.

The oil used in this investigation was extracted from the crushed fruits by light petroleum. The insoluble yellow solid matters were removed, the oil freed from the solvent and dried. Thus isolated, the oil has a yellow colour, a pleasant smell and a bitter taste. The following constants were recorded with a sample of dry oil.

Density at 31·5° (water at 31·5°)	...	0·9156
Refractive index at 40°	...	1·4691
Specific rotation in chloroform at 30° (11·29% soln.)	...	+ 1·04°
Solubility in alcohol at 25°	...	2·55%
Thermal value	...	16°
True Valenta number (acetic acid)	...	74·67°
Maumene test	...	95·06
Bromide test	...	nil
Acid value	...	16·6
Saponification value		189·62
Ester value	...	173·02
Iodine value (Wijs)	...	90·73
Hypochlorous acid value*	...	19·05
Acetyl value	...	23·56
Reichert-Meisl value (5 g. oil)	...	1·81
Polenske value (5 g. oil) .	...	0·25
Total saturated fatty acids (corr.)	...	14·02%
„ unsaturated „ „ „	...	78·08%
Unsaponifiable matter	...	1·96%

* Goswami and Basu, *J. Indian Chem. Soc.*, 1934, **11**, 905.

P. K. BOSE AND S. N. DUTT

An attempt has been made to correlate the above data and explain their significance. The thermal value and Maumene test indicate that the oil is non-drying. This inference is further supported by the iodine value. The solubility of the oil in alcohol is apparently due to the presence of glycerides of hydroxy-acids and the high acetyl value lends support to this suggestion. The low Reichert and Polenske values may be due to rancidity and decomposition. As a matter of fact high acid value is associated with rancidity. The absence of tetra-, hexa-, and octa-bromides in the bromination products of the total fatty acids indicates absence of polyunsaturated acids, although it should be mentioned that small quantities of higher unsaturated acids may escape detection by this method which is never quantitative in character.

The 'solid' saturated acids (yield 17 5%), obtained by the lead salt-ether method, had an iodine value of 20 showing that appreciable quantities of unsaturated acids are present along with the 'saturated' acids. A repetition of the process of separation did not much alter the I V. It is, therefore, evident that the 'saturated' acids must contain some unsaturated acids like erucic or petrosilenic acid, the lead salts of which are insoluble in ether and consequently they group together with the 'saturated' acid fraction It is noteworthy that petrosilenic acid has been found to occur in the seed oil of some plants belonging to the same Natural Order as *F. alliacea* (Dean, "Utilization of Fats," 1938. p. 93).

The alcoholysis of the oil was carried by the method described by Goswami and Ramanujam (*J. Indian Chem. Soc.*, 1931, **8**, 413). The methyl esters from 50 g. of the oil gave the following fractions on distillation at 16 mm.*

Fractions	...	I.	II.	III.	IV.	V
B.p.	...	Up to 100°	100-130°	130-155°	155-210°	210-20°
Yield	. .	0·85	0·42	2 4	0	32·2 g.

Fraction I consisted mainly of essential oil. Fractions II and III were not further examined for want of sufficient material. Myristic acid (b.p. of methyl ester, 167°/15 mm.) and palmitic acid (b.p. of methyl ester, 196°/15 mm.) are apparently absent. Fraction V, which constituted the bulk of the distillate, had an I.V. of 86·16 and gave no solid product on bromination of the acid obtained from this fraction. The b.p. as also the I.V. is in agreement with those of methyl oleate.

* During fractionation yellow solids separated out from the distilling liquid.

The natural coumarins present in *F. alliacea* as also the volatile oil will form the subject of a future communication.

E X P E R I M E N T A L.

Preliminary Experiments.—The fruits of *F. alliacea* were obtained from Poona. They were identified by Dr. K. Biswas of the Royal Botanic Garden, Sibpur and by Professor A. Das-Gupta, Calcutta, to both of whom we are greatly indebted. The fruits were coarsely powdered and 50 g out of the whole lot were successively extracted with different solvents in a Soxhlet. The solvents were removed in each case and the nature and quantities of the extracts were noted.

(*i*) Petroleum ether (b.p. 30—50°) extracted 20% of the material. The extract was a yellow oil containing a granular yellow solid, which amounted to nearly 1·2% of the fruits.

(*ii*) The ether extract was a brownish oil having little solid matter and amounted to 1·4%.

(*iii*) The chloroform extract (yield 2%) had a similar appearance.

(*iv*) The alcoholic extract (yield 3·7%) was a dark greyish brown tarry mass.

Extraction of the Oil.—For a large scale extraction, light petroleum was used and the extraction was continued briskly during 20 hours in a Soxhlet apparatus. The solvent was then removed on the water-bath and finally under reduced pressure in a slow current of air at about 70°. The oil was allowed to stand at room temperature for several days when a yellow granular solid separated out The oil was separated by filtration and dried over anhydrous sodium sulphate during a week. The clear oil, thus obtained, was used in the following experiments (yield 19%).

Essential Oil.—A portion of the above oil was distilled in steam. The distillate was taken up with ether, dried over sodium sulphate and the solvent removed under reduced pressure. The pale yellow oil thus obtained (yield 0·9%) had a pleasant camphoraceous smell.

Thermal Value (Bromine Thermal Test).—This test is a measure of the heat evolved on treating a definite weight (1 g.) of an oil dissolved in a definite volume (10 c.c.) of chloroform with a definite (1 c.c.) volume of bromine. The test was carried out in a Dewar's flask.

Initial temp. of oil and chloroform	...	32°
Final temp. after addition of bromine		48°
Hence thermal value	...	16°

True Valenta Number (Acetic Acid).—It was determined by the method of Freyer and Weston ("Handbook of Oils, Fats and Waxes," 1918, Vol. I, p. 76).

Turbidity temp. of oil	...	54 5°
Oleic acid content	...	8·61%
Corrected turbidity temp.	...	74·04°
Turbidity temp. of almond oil	...	72·5°
Oleic acid content	·	3·03%
Corrected turbidity temp.	·	79 37°
Hence true Valenta number	...	74·67·

Maumene Test.—The modified method of Thompson and Ballantyne (*J. Chem. Soc. Ind.*, 1891, 234) was followed.

Initial temp. of oil	...	26°
Final temp. after treatment	...	64·5°
Hence rise of temp.	...	38·50°
Initial temp. of water	..	26°
Final temp. after mixing with H_2SO_4	...	66·5°
Hence rise of temp.	...	40·5°
Therefore, Specific Temperature Reaction	=	95·06

Separation of Solid and Liquid Acids.—8 G. of the oil gave 1·393 g. of ' saturated ' acids and 5·969 g. of ' unsaturated ' acids. The I.V. of the ' saturated ' acid was found to be 19·9. Hence amount of monounsaturated acids present in the saturated acids = 3·48%. Therefore, corrected percentage of saturated acids = 14·02 and corrected percentage of unsaturated acids = 78·08.

The I.V. of the ' unsaturated ' acids was found to be 100·6. The ' saturated ' acids were obtained as an oil, which solidified on keeping and melted at 29-30°.

We are indebted to Dr. M. N. Goswami for some valuable suggestions in connexion with this investigation.

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APPLICATION OF BEER'S LAW OF ABSORPTION TO SOLUTIONS.

By W. V. BHAGWAT

Application of Beer's law to the solutions of potassium dichromate, picric acid, didymium nitrate, methyl violet, methylene blue. chromic acid, nickel nitrate, nickel sulphate, nickel chloride and cobalt chloride has been tested. It is observed that nickel chloride and cobalt chloride behave similarly to cupric chloride and does not obey Beer's law While solutions of other substances follow the law more or less approximately, deviation being greater as the concentrations become widely separated. The results also indicate that ionisation alone is not responsible for deviation from Beer's law.

According to Beer's law when an absorbing substance is in the gaseous state or dissolved in a transparent solvent, the absorption coefficient is proportional to the concentration. Thus $e = k\,c$.

It is well known that the law is valid only in case of monochromatic radiations and when the molecular characteristic of the dissolved substance does not change with dilution The law does not hold good in the case of cupric chloride solution due to the formation of complex ions. Thus :—

$$CuCl_2 \longrightarrow CuCl^{\cdot} + Cl$$
$$CuCl' \longrightarrow Cu^{\cdot\cdot} + Cl''$$
$$CuCl_2 + Cl' \longrightarrow CuCl_3'$$
$$CuCl_3' + Cl' \longrightarrow CuCl_4''$$

However, the law is applicable in case of potassium permanganate and others (cf. Dhar, "Chemical Action of Light", p. 17).

In this paper an attempt has been made to investigate the applicability of this law to various solutions in various regions of the visible spectrum. The amount of absorption and extinction coefficients for different concentrations were determined with the help of Nuttings photometer combined with constant deviation spectrometer. The regions compared were not strictly monochromatic due to the width of the slit of the telescope, although they were identical for all solutions. The width of the region was about 200Å. The observed results together with those calculated on the basis of proportionality between e and c are given below. It is assumed that the observed values for the lowest concentrations are the true values and on this basis expected values at other concentrations are calculated. This principle is separately followed in each table.

The thickness of the solution in all cases was 1 cm. Concentrations were expressed either as mols per litre or number of grams in a given volume or in terms of normality $= \dfrac{\text{Molecular weight}}{\text{Basicity of the salt}}$. $e =$ observed extinction coefficient, $e_c =$ calculated value of extinction coefficient. $l =$ wave length in Å units.

TABLE I.

Potassium dichromate.

Conc.		5400Å.	5500Å	5600Å	5800Å.	6000Å.
0·0513 M	e	0·25	0·10	—	0·04	0·02
,,	e_c	0·25	0·10	—	0·04	0·02
0·256	e	1·32	0·52	0·20	—	—
,,	e_c	1·25	0·50	0·20	—	—
0·513	e	2·8	1·06	0·40	0·14	0·04
,,	e_c	2·5	1·00	0·40	0·40	0·20

It appears from these results that in regions where absorption is appreciable ($\lambda = 5400$Å, 5500Å and 5600Å) Beer's law is more or less applicable for all the concentrations examined. When, however, the extinction coefficient becomes small ($\lambda = 5800$ Å and 6000 Å) the law is not valid. It is to be further observed that the deviation becomes more marked as the concentrations differ more and more from one another. Thus the results when 0·256 M and 0·513 M solutions of potassium dichromate are alone compared are in better agreement than when all the solutions are compared together. This is obvious, because when change in concentration is small, the deviation is also small.

TABLE II.

Picric acid.

Conc. (g./100 c.c.)		4850Å.	5000Å.	5180Å.
0·666	e	0·60	0·09	0·03
,,	e_c	0·60	0·09	0·03
1·333	e	1·05	0·17	0·07
,,	e_c	1·20	0·18	0·06

For the concentrations examined the Beer's law seems to be applicable in cases of picric acid.

TABLE III.

Didymium nitrate.

Conc. (g./100 c c.)		4370Å.	4400Å.	4470Å	4590Å
22·687	e	0·19	0·19	0·21	0·52
,,	e_c	0 19	0·64	0·21	0·52
45·375	c	0·35	1·19	0·40	0·58
,,	e_c	0·38	1·28	0·42	0 67

		4640Å.	4720Å.	4850Å.	5000Å.	5020Å.
22 687	e	0·41	0·26	0·05	0·47	0·50
,,	e_c	0·41	0·26	0·05	0·47	0·50
45·375	e	0·72	0·49	0·07	0·79	1·03
,,	e_c	0·82	0·52	0·10	0·94	1·00

		5100Å.	5180Å.	5380Å.	5640Å	5870Å.	6540Å
22·678	e	0·74	0·29	0·04	1·65	0·02	0·11
,,	e_c	0·74	0·29	0·04	1·65	0·02	0·11
45·375	e	1·27	0 57	0·07	2·25	0 03	0 18
,	e_c	1·48	0·58	0·08	3·30	0·04	0·22

The absorption by didymium nitrate is known to be peculiar. It shows various regions of maximum absorptions (*cf.* Bhagwat and Dhar, *J. Phys. Chem.*, 1931, **35**, 2393), the centres of maxima being near about 4200 Å, 4640Å, 5000Å, 5020Å, 5100Å, 5640Å and 6540Å. The above results point out that Beer's law is more valid in regions other than those of maximum absorption.

The absorption of didymium nitrate at lower concentration has also been determined, but when the results are calculated on this basis the deviation from Beer's law is much marked. In other words, the deviation from Beer's law becomes more pronounced as the difference in concentration increases.

TABLE IV.

Conc. (g./100 c.c.)		4370Å.	4470Å.	4590Å.	4720Å.	4850Å	5000Å.	5180Å.	5640Å.	6540Å.
4.5375	e	0.05	0.05	0.07	0.06	0.02	0.10	0.07	0.40	0.03
,,	e_e	0.05	0.05	0.07	0.06	0.02	0.10	0.07	0.40	0.03
22.687	e	0.19	0.21	0.32	0.26	0.05	0.47	0.29	1.65	0.11
,,	e_e	0.25	0.25	0.35	0.36	0.10	0.50	0.35	2.00	0.15
45.375	e	0.35	0.40	0.58	0.49	0.07	0.79	0.57	2.25	0.18
,,	e_e	0.50	0.50	0.70	0.60	0.20	1.00	0.70	4.00	0.30

The results clearly show that the deviation from Beer's law is appreciable for the higher concentrations (45.375 g.) than for the concentration (22.687). Beer's law therefore is not valid in this case when the concentrations compared are widely apart. It is to be further observed that this deviation is much greater in the regions where absorption is very low and also very high.

TABLE V.

Methyl violet.

Conc. (g./100 c.c.)		6540Å.	6160Å.	4850Å.	4720Å.	4590Å.	4470Å.	4370Å.	4280Å.
0.0020	e	—	0.09	0.27	0.19	0.14	0.12	0.12	—
0.010	e	0.03	0.44	2.00	1.32	0.76	0.52	0.35	—
0.025	e	0.07	0.80	—	1.85	1.85	1.12	0.75	0.50
0.050	e	0.12	1.50	—	—	—	1.85	1.22	0.76
0.100	e	0.23	—	—	—	—	—	1.95	1.5

It seems that Beer's law is not applicable in the case of methyl violet solutions. The law is not approximately valid even when the absorption of similar concentrations, such as 0.050 and 0.100 g. in 100 c.c. or 0.025 g. and 0.050 g. in 100 c.c. are compared with one another. In view of the fact that these dyes behave as colloids the deviation from Beer's law at high dilutions is as expected, since the molecular complexity changes with dilution.

TABLE VI.

Methylene blue.

Conc. (g./100 c.c.)		5380Å.	5180Å.	5000Å.	4850Å.	4720Å.	4590Å.	4470Å.
0·0116	e	1·46	1·08	0·86	0·72	0·54	0·34	0·27
,,	$e_{\bullet}$	1·46	1·08	0·86	0·72	0·54	0·34	0·27
0·0232	e	2·6	2·05	1·70	1·38	1·04	0·84	0·66
,,	$e_{\bullet}$	2·92	2·16	1·72	1·44	1·08	0·78	0·54

The results indicate that for the two concentrations examined Beer's law seems to be valid in the case of methylene blue.

TABLE VII.

Chromic acid.

Conc.		5600Å.	5870Å.	6160Å.	6540Å.
1·416 N	e	0·58	0·27	0·23	0·15
,,	$e_{\bullet}$	0·58	0·27	0·23	0·15
2·833	e	1·44	0·50	0·38	0·25
,,	$e_{\bullet}$	1·16	0·54	0·46	0·30
5·666	e	—	1·38	0·86	0·50
,,	$e_{\bullet}$	—	1·08	0·92	0·60

Beer's law seems to be fairly applicable in the case of chromic acid for the concentrations examined. As in previous cases the related concentrations show better agreement than the concentrations which are widely apart.

TABLE VIII.

Nickel nitrate.

Conc.		4400Å.	4600Å.	4800Å.	5000Å.	5200Å.	5400Å.	5600Å.	5800Å.	6000Å.
0·208 M	e	0·16	0·10	0·06	0·04	0·05	0·05	0·05	0·09	0·16
,,	$e_{\bullet}$	0·16	0·10	0·06	0·04	0·05	0 05	0·05	0·09	0·16
1·04	e	0·82	0·55	0·30	0·30	0·25	0·27	0·27	0·28	0·47
,,	$e_{\bullet}$	0·80	0·50	0·30	0·20	0·25	0·25	0·25	0·45	0 80
2·08	e	1·65	1·20	0·57	0·52	0·55	0·57	0·60	0·96	1·70
,,	$e_{\bullet}$	1·60	1·00	0·60	0·40	0·50	0·50	0·50	0·90	1·60
4·16	e	—	2·45	1·30	1·10	1·17	1·20	1·25	1·95	4·45
,,	$e_{\bullet}$	—	2·00	1·20	0·80	1·00	1·00	1·00	1·80	3·20

Considering the wide range (4˙16 M to 0˙208 M) examined the results are fairly in agreement with the Beer's law. If the concentrations 1˙04 M, 2˙00 M and 4˙16 M are alone compared the validity of the law is excellent.

TABLE IX.

Nickel nitrate.

Conc.		6200Å.	6400Å.	6600Å.	7000Å.
0·208 M	e	0·29	0·36	0·40	0·45
,,	$e_,$	0·29	0·36	0·40	0·45
1·04	e	—	1·90	2·20	2·45
,	$e_,$	—	1·80	2·00	2·20
2·08	e	3·0	—	—	—
,,	$e_,$	2·9	—	—	—
4·16		—	—	—	—
,,		—	—	—	—

TABLE X.

Nickel sulphate.

Conc.		4600Å.	4800Å.	5000Å.	5200Å.	5400Å.	5600Å.	5800Å.	6000Å.	6200Å.	6400Å.
0·93 N	e	0·10	0·08	0·05	0·08	0·10	0·15	0·17	0·30	0·55	0·70
2·30	e	0·32	0·17	0·10	0·17	0·20	0·30	0·42	0·70	1·25	1·70
5·28	e	0·90	0·48	0·27	0·40	0·50	0·65	1·05	1·65	2·35	—

These results show that deviation from Beer's law becomes more marked as the concentration differences increase. Nickel salts show high absorption at both ends of the visible spectrum. It will be observed that as these regions are approached, specially at high concentrations, the deviation from Beer's law becomes still enhanced.

TABLE XI.

Nickel chloride.

Conc.		6200Å.	6000Å.	5800Å.	5600Å	5400Å.	5200Å.	5000Å.	4800Å.
0·926 N	e	0·57	0·36	0·27	0·22	0·18	0·16	0·16	0·23
4·63	e	2·0	1·38	0·88	0·60	0·46	0·40	0·37	0·58
9·26	e	—	2·0	1·36	1·02	0·84	0·77	1·04	3·0

Beer's law completely breaks down in this case. The law fails even when the concentrations 4˙63 N and 9˙26 N alone are compared. It seems that nickel chloride behaves in a very similar manner to cupric chloride. It is most likely that complexes of the nature $NiCl_3'$ $NiCl_4''$ etc , like $CuCl_2'$, $CuCl_4''$ are formed in solution.

TABLE XII.

Cobalt chloride.

Conc.		7000Å.	6600Å.	6200Å.	6000Å.	5800Å.	5400Å	4600Å.	4400Å.
0˙183 M	e	0˙05	0˙07	—	0˙08	—	0˙55	0˙59	0˙35
0˙915	e	0˙32	—	0˙46	—	0˙73	3˙75	3˙15	1˙6
1˙83	e	—	0˙82	0˙85	1˙05	1˙70	—	—	3˙75

The law does not seem to be applicable in case of cobalt chloride.

All these results point out that merely increase in the degree of ionisation does not affect Beer's law. Thus Beer's law is more or less applicable in the case of potassiun dichromate, picric acid, didymium nitrate chromic acid, nickel nitrate and nickel sulphate for the concentrations examined.

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VELOCITY OF TRANSFORMATION OF 1 : 3 : 5-TRIKETONES INTO 2 : 6-DISUBSTITUTED γ-PYRONES. PART I. VELOCITY OF TRANSFORMATION OF ACETONE DIOXALIC ESTER INTO CHELIDONIC ESTER.

By S. S. Deshapande, W. V. Bhagwat and C. W. Subnis.

In order to investigate the structure of 1·3:5-triketones by physical method acetone dioxalic ester is chosen as the standard substance of comparison as its constitution is definitely known. Velocity constants of the change of this ester into chelidonic ester are given and the mechanism of the change explained.

Deshpande, Dingankar and Kopil (*J. Indian Chem. Soc.*, 1934, **11**, 595) described the synthesis of dipropionylacetone and di-*n*-butyryl-acetone. The reactions of the products led the authors to assign the structure (I, R=C_2H_5 or C_3H_7) to these compounds.

$$R \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot R \quad (I)$$

By analogy diacetylacetone should be (I, R =CH_3). The simple structure (I, R=CH_3) is, however, opposed to Collie's structure for diacetylacetone (II), based on the chemical relations of this compound to dimethylpyrone which he represents by the oxide structure formed by the loss of a molecule of water (*J. Chem. Soc.*, 1904, **85**, 971).

(II)

Deshapande, Bedekar and Kaushal (*J. Indian Chem. Soc.*, 1935, **12**, 465) have given additional evidence in support of the open-chain structure (I, R=CH_3) for diacetylacetone and its homologues. They have shown that γ-pyrone and 2 : 6-substituted γ-pyrones have probably simple ring structure (III) rather than the bridge ring structure assumed by Collie.

$$
\begin{array}{cc}
\text{(III)} & \text{(V)}
\end{array}
$$

(III) — ring structure: CO at top, HC / CH, R–C / C–R, O at bottom

(V) — structure: CO$_2$Et, CH=C, OC, CH=C, O, CO$_2$Et

      (III)   (V)

In the present paper an attempt has been made to throw more light on the structure of these substances by physicochemical investigations.

The plan adopted was to make a comparison between diacetylacetone or its higher homologues and an open-chain 1:3: 5-triketone, *e.g.* acetone dioxalic ester (IV), synthesised by Claisen from acetone and oxalic ester in two stages.

$$CO_2Et \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et \quad \text{(IV)}$$

It is well known that acetone dioxalic ester under dehydrating conditions such as keeping in vacuum, loses a molecule of water and changes into the ring compound, chelidonic ester (V). The substance (acetone dioxalic ester) exists in monoenol and dienol forms, the dehydration taking place from the dienol form.

It has been found that for this reaction dehydrating conditions are not necessary. Acetone dioxalic ester dissolves in any non-dehydrating medium such as acetone or dilute alcohol and changes into chelidonic ester in the presence of a trace of a catalyst. It is further found that this relation is quantitative and is accompanied by no side-reactions and is one of the few reactions which are strictly unimolecular.

EXPERIMENTAL.

Acetone dioxalic ester was crystallised from glacial acetic acid and dried at low temperature, m.p. 100-101°. The rate of transformation was investigated by physical and chemical methods.

The known weight of acetone dioxalic ester was dissolved in a known volume of the solvent containing a known concentration of the catalyst and the reaction was carried in a thermostat at a fixed temperature. At definite intervals, a known volume of the solution was pipetted and three times the volume of water added to it. Under these conditions the chelidonic ester is completely soluble, while acetone dioxalic ester being almost insoluble, is completely precipitated. The slight correction for the solubility of the ester was introduced by determining its solubility in the mixed solvent used at the time of precipitation. From the corrected weight of the unchanged ester the rate of the chemical change was determined.

In the chemical method unchanged acetone-dioxalic ester was determined from time to time by precipitating it as insoluble copper salt with copper acetate solution. The copper salt of acetone dioxalic ester is quantitatively precipitated if to a dilute methyl or ethyl alcoholic solution of the compound aqueous copper acetate is added and under these conditions chelidonic ester remains in solution.

TABLE I.

Solvent—Acetone ; Catalyst—0·015N-HCl. Temperature—22°. Weight of acetone dioxalic ester—4·0152 g. Volume of solution—50 c.c. Volume of the solution withdrawn each time—3 c.c. Water added—12 c.c. Solubility correction - 0·0192 g in 15 c c. of mixed solution.

Time (t).	Wt. of unchanged triketone.	Unchanged wt. (corrected).	$k_1 = \frac{1}{t} \log \frac{a}{(a-x)}$
o min.	0·2130 g.	0·2322 (a)	—
29	0·1928	0·2120 (a−x)	0·00134
59	0·1710	0·1902	0·00134
108	0·1476	0·1668	0·00134
149	0·1282	0·1474	0·00133
211	0·1018	0·1210	0·00134
269	0·0824	0·1016	0·00133
361	0·0574	0·0766	0·00133

TABLE II.

Solvent—Acetone. Catalyst—0·0432N-HCl. Temperature—52°. Weight of the ester—2·7690 g. Solubility of the ester in 15 c.c. of the mixed solvent at 52°—0·0233. Other factors same as in Table I.

Time (t).	Unchanged ester.	Unchanged ester (corrected).	$k_1 = \frac{1}{t} \log \frac{a}{a-x}$.
o min.	0·1428	0·1661 (a)	—
10	0·1146	0·1379 (a−x)	0·0081
29	0·0738	0·0971	0·0080
45	0·0466	0·0699	0·0083
61	0·0278	0·0511	0·0084
80	0·0090	0 0323	0·0088
97	0·0010	0·0243	0·0086

TABLE III.

Chemical method.

Reaction was very rapid at 54°. Solvent—50% aqueous methyl alcohol. Strength of HCl—0·0402 N. Temperature—54°. Weight of ester—0·1634g. Volume of the solution—96 c.c. Volume of the solution precipitated as copper salt each time—20 c.c.

Time (t).	Wt. of Cu salt.	$k_1 = \frac{1}{t} \log \frac{a}{a-x}$.
0 min.	0·0393	—
5	0·0270	0·0325
23	0·0070	0·0325

These results clearly show the unimolecular nature of the transformation of acetone dioxalic ester into chelidonic ester.

DISCUSSION.

Acetone dioxalic ester exists as an equlibrium mixture in solution of its keto-enolic forms since it is the enolic form which undergoes dehydration into chelidonic ester :

If C_1 and C_2 are their respective concentrations at equilibrium then

$$\frac{C_2}{C_1} = \text{constant } (m) \qquad \qquad \ldots \ (i)$$

Again the enolic form changes into chelidonic ester which is one-sided reaction as the change goes to completion

If $a-x$ is the concentration of enol form at any time t, initial concen- being a, then,

$$\frac{dx}{dt} = k(a-x) \qquad \qquad \ldots \ (ii)$$

Thus we have to consider both the reactions simultaneously.

Let a be the initial concentration of keto form and b, be the concentration of enol form at any time t and x be the change in concentration of the

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enol form in the same time t, then the concentration of unchanged keto form at the same time is $a-b-x$.

But by equation (i) $\dfrac{b}{a-b-x}=m.$

Therefore, the concentration of b, at any time t is given by

$$b=m(a-b-x)=ma-mx-mb$$

or $$b+mb=ma-mx$$

or $$b(1+m)=m(a-x) \quad \text{or} \quad b=\frac{m}{1+m}(a-x).$$

Thus $\dfrac{dx}{dt}$ for one sided-reaction is given by

$$\frac{dx}{dt}=k\ \frac{m}{1+m}\ (a-x).$$

but m is a constant.

Hence $$\frac{dx}{dt}=k_1\ (a-x)$$

or $$k_1=\frac{1}{t}\ \log\frac{a}{a-x}$$

or the whole change is represented by unimolecular equation. Our results confirm the above mechanism of the reaction.

SYNTHESIS OF COUMARINS FROM O-HYDROXY-ARYL-ALKYL KETONES. PART III.

BY DUHKHAHARAN CHAKRAVARTI AND NARENDRALAL DUTTA.

In continuation of the new method of synthesis of coumarins from o-hydroxy-aryl-alkyl ketone it has been found that when there is an alkyl substituent in the β-position of the expected cinnamic ester coumarin is invariably formed irrespective of the presence of any substituent in the α-position, the presence of any alkyl group or a halogen atom in the benzene nucleus of the ketone having without any appreciable effect on the reaction. Thus 4-alkylcoumarins and 3 : 4-dialkylcoumarins have been prepared in excellent yield.

The o-hydroxyaryl-alkyl ketones have been conveniently used by Chakravarti and Majumdar (*J. Indian Chem. Soc.*, 1938, **15**, 136) for the synthesis of coumarin derivatives. They have also observed that o-methoxy-benzaldehyde, 5-chloro-o-methoxybenzaldehyde and β-resorcylaldehyde dimethyl ether, when condensed with ethyl bromoacetate or ethyl α-bromo-propionate form o-coumaric acid derivatives which do not lactonise readily (*J. Indian Chem. Soc.*, 1939, **16**, 389).

The present investigation has been undertaken with a view (i) to study the effect of various substituents, e.g. alkyl, Cl, Br, etc., in different positions in the phenyl nucleus of the o-hydroxy-aryl-alkyl ketones on the formation of coumarins.

(ii) and secondly to study the influence of substituents in the α-and β-positions of the cinnamic ester to be formed on the formation of o-coumaric acids in the above synthesis.

The methoxy derivatives of the following ketones, viz., 5-chloro-2-hydroxy-, 5-bromo-2-hydroxy-, 3-methyl-2-hydroxy-, 5-methyl-2-hydroxy-, 5-chloro-3-methyl-2-hydroxy-, 5-chloro-4-methyl-2-hydroxy-, 5-methyl-3-chloro-2-hydroxy-acetophenones, 5-chloro-3-methyl-2-hydroxy-, 3-chloro-5-methyl-2-hydroxy-propiophenones have been condensed with ethyl bromo-acetate and ethyl-α-bromopropionate according to Reformatsky forming hydroxy-esters, which are treated with thionyl chloride and pyridine to yield unsaturated esters. The latter on treatment with hydriodic acid or on keeping with concentrated sulphuric acid (d 1·84) overnight give quanti-tative yields of the coumarins. It is not absolutely necessary to convert the hydroxy-esters into the unsaturated esters and the former may as well be conveniently utilised for the lactonisation to form coumarins.

The acetophenones and the propiophenones have all been prepared from the corresponding acetyl and the propionyl derivatives of the phenols by

heating with aluminium chloride (Fries rearrangement). It has been obser-
ved that in some cases an appreciable amount of phenol results, obviously
from the deacetylation or depropionylation of the acetyl or propionyl deri-
vatives as the case might be. The formation of the phenol is effectively
overcome by heating with aluminium chloride for half an hour at 130-40°.

Some of the coumarins, synthesised by this method, have been found
to be identical (m.p. and mixed m.p.) with the compounds described by
Chakravarti and Banerjee (*J. Indian Chem. Soc.*, 1936, **13**, 619) by the
application of Pechmann's reaction on the phenols or by Chakravarti and
Majumdar (*ibid.*, 1939, **16**, 151) by Kostanecki's reaction on *o*-hydroxy-
acetophenones.

It is evident, therefore, that when there is an alkyl substituent in the
β-position of the expected cinnamic ester, coumarin is invariably formed,
irrespective of the presence of any substituent in the α-position. Thus 4-
alkylcoumarins and 3:4-dialkylcoumarins may readily be synthesised from
the appropriate *o*-hydroxy-aryl-alkyl ketones, the presence of any alkyl
group or a halogen atom in the benzene nucleus of the ketone having without
any appreciable effect on the reaction.

EXPERIMENTAL.

5-Chloro-2-methoxyacetophenone.—A solution of 5-chloro-2-hydroxy-
acetophenone (20 g.) in alcoholic sodium ethoxide (2·7g. of sodium in 60 c.c.
of alcohol) was heated on the water-bath with methyl iodide (20 g.) for
about 3 hours. The excess of alcohol was distilled off and the methoxy
derivative was extracted with ether, the ethereal extract washed with a
dilute solution of caustic soda and then with water, dried and distilled. It
was obtained as a colourless thick oil, b.p. 135°/6 mm. It solidifies on
chilling in ice. (Found: Cl, 19·24. $C_9H_9O_2Cl$ requires Cl, 19·24 per cent).

Ethyl 2 Methoxy-5-chloro-β-methylcinnamate.—A mixture of 2-
methoxy-5-chloroacetophenone (7 g.), ethyl bromoacetate (11 g.), zinc-wool
(5 g.) and benzene (25 c.c.) was heated on a water-bath for 2-2½ hours, when
the zinc dissolved. The solution was then poured into ice-cold dilute
sulphuric acid, the benzene layer was separated, washed with dilute sodium
carbonate solution and with water and then dried. On removing benzene it
was distilled at 155-60°/5 mm. as a thick light yellow oil, yield 6·5 g. The
hydroxy-ester (6·5 g.) was converted into the unsaturated ester with thionyl
chloride (2·5 c.c.) in presence of pyridine (3 c.c.) in dry ethereal solution
(100 c.c.). After decomposing excess of thionyl chloride with ice the ethereal
layer was washed with dilute hydrochloric acid, sodium carbonate and
finally with water. On removing ether the product was distilled at 155°/5 mm,

Table I.

Name of the compound.	Mol. formula.	Prepared from	Analysis Found.	Analysis Theo.	M.p. or B.p.	Remarks.
5-Bromo-2-methoxy-acetophenone. (I)	C₉H₉O₂Br	5-Bromo-2-hydroxy-acetophenone	Br, 34·94	34·93	165°/12 mm.	Colourless thick oil
Ethyl 2-methoxy-5-bromo-β-methylcinnamate (IIa)	C₁₃H₁₅O₃Br	(I) and ethyl bromoacetate and then dehydrated	26·71	26·75	180°/8 mm.	Colourless oil
4-Methyl-6-bromocoumarin.	C₁₀H₇O₂Br	(IIa) using H₂SO₄	33·37	33·47	187°	Needles from spirit
Ethyl 2-methoxy-5-bromo-αβ-dimethylcinnamate. (IIb)	C₁₄H₁₇O₃Br	(I) and ethyl α-bromopropionate and then dehydrated	Br, 25·26	25·55	169-70°/10 mm.	Colourless oil
3:4-Dimethyl-6-bromocoumarin	C₁₁H₉O₂Br	(Ib) using H₂SO₄	31·71	31·58	169°	Needles from dilute alcohol
*3-Methyl-2-methoxy-acetophenone (II)	C₁₀H₁₂O₂	3-Methyl-2-hydroxy-acetophenone	C, 73·2 H, 7·5	73·17 7·3	120°/3 mm.	Colourless oil
*Ethyl 2-methoxy-3-methyl-β-methylcinnamate (IIa)	C₁₄H₁₈O₃	(II) and ethyl bromoacetate and then dehydrated	C, 71·61 H, 7·7	71·79 7·69	140-42°/9 mm.	Colourless oil
*4:8-Dimethylcoumarin	C₁₁H₁₀O₂	(IIa) using H₂SO₄	C, 76·13 H, 5·9	75·86 5·74	114°	Crystallised from dilute alcohol as needles
*5-Methyl-2-methoxy-acetophenone (III)	C₁₀H₁₂O₂	5-Methyl-2-hydroxy-acetophenone	C, 73·11 H, 7·2	73·17 7·3	110°/6 mm.	Colourless oil

as a colourless oil, yield 3 g. (Found: Cl, 14·06. $C_{13}H_{15}O_3Cl$ requires Cl, 13·94 per cent).

4-Methyl-6-chloro-coumarin.—The above unsaturated ester (1 g.) was kept overnight with sulphuric acid (d 1·84, 6 c.c.). The solution was treated with powdered ice and the solid obtained was crystallised from methyl alcohol, m.p. 184°, yield quantitative. The ring-closure was also effected by heating the unsaturated ester with hydriodic acid (d 1·7, 6 c.c.) at 140° for 2 hours. (Found: Cl, 18·58. $C_{10}H_7O_2Cl$ requires Cl, 18·25 per cent). The coumarins described in this paper were all prepared in the above way and they are described in Table I

TABLE I (contd.).

Name of the compound.	Mol. formula.	Prepared from	Analysis Found.	Analysis Theo.	M.p. or B.p.	Remarks.
*Ethyl 2-methoxy-3-methyl-β-methylcinnamate (IIIa)	$C_{14}H_{18}O_3$	(III) and ethyl bromoacetate and then dehydrated	C, 71·54 H, 7·79	71·79 7·69	160°/12 mm	Colourless oil
4:6-Dimethylcoumarin	...	(IIIa) using H_2SO_4			150°	Identical with the compound described by Chakravarti and Banerjee (loc. cit.)
*Ethyl αβ-dimethyl-β-hydroxy-β(2-methoxy-5-methyl)-phenyl propionate (IIIb)	$C_{15}H_{22}O_4$	(III) and ethyl α-bromopropionate	C, 67·83 H, 8·06	67·67 8·27	140-45°/8 mm	Colourless oil
3:4:6-Trimethylcoumarin	...	(IIIb) using H_2SO_4	...	...	170°	Identical with the compound described by Chakravarti (J. Indian Chem. Soc., 1932, 9, 29) (mixed m.p.)
5-Chloro-3-methyl-2-methoxypropiophenone (IV)	$C_{11}H_{13}O_2Cl$	5-Chloro-3-methyl-2-hydroxypropiophenone (Chakravarti and Majumdar, J. Indian Chem. Soc., 1939, 16, 155)	Cl, 16·6	16·7	139°/8 mm	Oil with a yellow tinge
Ethyl 2-methoxy-3-methyl-5-chloro-α-methyl-β-ethylcinnamate (IVa)	$C_{16}H_{21}O_3Cl$	(IV) and ethyl α-bromopropionate and then dehydrated	Cl, 12·3	11·96	164°/6 mm	Colourless oil
3:8-Dimethyl-4-ethyl-6-chlorocoumarin	$C_{13}H_{13}O_2Cl$	(IVa) using H_2SO_4 or HI	Cl, 15·17	15·1	126°	Fine needles from dilute alcohol
3-Chloro-5-methyl-2-methoxypropiophenone (V)	$C_{11}H_{13}O_2Cl$	3-Chloro-5-methyl-2-hydroxypropiophenone	Cl, 16·5	16·7	140°/8 mm	Colourless oil

TABLE I (contd).

Name of the compound.	Mol. formula.	Prepared from	Analysis Found.	Analysis Theo.	M.p. or B.p.	Remarks.
Ethyl 2-methoxy-3-chloro-5-methyl-α-methyl-β-ethylcinnamate (Va)	$C_{16}H_{21}O_3Cl$	(V) and ethyl α-bromopropionate and then dehydrated	Cl, 12·0	11·96	160°/8 mm.	Colourless oil
3:6-Dimethyl-4-ethyl-8-chlorocoumarin	$C_{13}H_{13}O_2Cl$	(Va) using H_2SO_4 or HI	Cl, 15·1	15·01	120°	Needles from dilute alcohol
5-Chloro-3-methyl-2-methoxyacetophenone (VI) (Chakravarti and Majumdar, loc. cit.)	$C_{10}H_{11}O_2Cl$		Cl, 17·7	17·8	136°/8 mm.	Light yellow oil
Ethyl 2-methoxy-3-methyl-5-chloro-β-methylcinnamate (VIa)	$C_{14}H_{17}O_3Cl$	(VI) and ethyl bromoacetate and then dehydrated	Cl, 13·4	13·2	163°/5 mm.	Colourless oil
4:6-Dimethyl-6-chlorocoumarin	$C_{11}H_9O_2Cl$	(VIa) using H_2SO_4	Cl, 17·5	17·02	155°	Needles from dilute alcohol
Ethyl 2-methoxy-3-methyl-5-chloro-αβ-dimethylcinnamate (VIb)	$C_{15}H_{19}O_3Cl$	(VI) and ethyl α-bromopropionate and then dehydrated	Cl, 12·8	12·56	165°/7 mm.	Colourless oil
3:4:8-Trimethyl-6-chlorocoumarin		(VIb) using H_2SO_4 or HICl			114°	Identical with the compound described by Chakravarti and Majumdar (loc. cit.) (mixed m.p.)

† The m.p. of the compound as recorded by Chakravarti and Majumdar (m.p. 94°) was found to be incorrect as the m.p. rose to 114° on recrystallisation.

TABLE I (contd.).

Name of the compound.	Mol. formula.	Prepared from	Analysis Found.	Theo.	M.p. or B.p.	Remarks.
5-Chloro-3-methyl-2-methoxyacetophenone (VII)	$C_{10}H_{11}O_2Cl$	5-Chloro-3-methyl-2-hydroxyacetophenone	Cl, 17·7	17·8	81°	Colourless, needles from dilute alcohol
Ethyl 2-methoxy-4-methyl-5-chloro-β-methylcinnamate (VIIa)	$C_{14}H_{17}O_3Cl$	(VII) and ethyl bromoacetate and then dehydrated	Cl, 13·8	13·2	160°/5 mm.	Colourless oil
4:7-Dimethyl-6-chlorocoumarin	...	(VIIa) using H_2SO_4 or HI	...	...	213°	Identical with the compound described by Chakravarti and Banerjee (loc. cit.) (mixed m.p.)
Ethyl 2-methoxy-4-methyl-5-chloro-αβ-dimethylcinnamate (VIIb)	$C_{15}H_{19}O_3Cl$	(VII) and ethyl α-bromopropionate and then dehydrated	Cl, 12·7	12·56	160°/3 mm.	Colourless oil
3:4:7-Trimethyl-6-chlorocoumarin	...	(VIIb) using H_2SO_4 or HI	...	...	†167°	Identical with the compound described by Chakravarti and Banerjee (loc. cit.) (mixed m.p.)
5-Methyl-3-chloro-2-methoxyacetophenone (VIII)	$C_{10}H_{11}O_2Cl$	5-Methyl-3-chloro-2-hydroxyacetophenone	Cl, 17·6	17·8	124°/4 mm.	Colourless oil

† The m.p. of Chakravarti and Banerjee's compound (recorded as 146°) rose to 167° on further crystallisation.

TABLE I (contd.).

Name of the compound.	Mol. formula.	Prepared from	Analysis Found.	Theo.	M.p. or B.p.	Remarks.
Ethyl 2-methoxy-3-chloro-5-methyl-β-methyl-cinnamate (VIIIa)	$C_{14}H_{17}O_3Cl$	(VIII) and ethyl bromoacetate and then dehydrated	Cl, 13·41	13·22	160°/6 mm.	Colourless oil
4:6-Dimethyl-8-chloro-coumarin.	...	(VIIIa) and H_2SO_4	...		148°	Identical with the compound described by Chakravarti and Banerjee (loc. cit.) (mixed m.p.)
Ethyl 2-methoxy-3-chloro-5-methyl-αβ-di-methylcinnamate (VIIIb)	$C_{15}H_{19}O_3Cl$	(VIII) and ethyl α-bromopropionate and then dehydrated	Cl, 12·59	12·56	170°/9 mm.	Colourless oil
3:4:6-Trimethyl-8-chloro-coumarin	...	(VIIIb) and HI	...		153°	Needles from dilute alcohol. Identical with the compound described by Chakravarti and Majumdar (loc. cit.) (mixed m.p.)

* The analyses of compounds marked with * are micro-analyses done by Mr. N. Ghosh of the University College of Science, to whom our best thanks are due.

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ECONOMICS OF COAL CARBONISATION.*

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My object in bringing the problem of coal carbonisation before you is to draw your attention to the limited coal deposits of India amounting barely to 1% of the world's total reserves, and the consequent economy necessary to organise a sound national fuel industry   The practice of coal carbonisation is comparatively recent, but the tendency to produce concentrated fuels by carbonising may be traced to the primitive man who started stack-burning of wood, to produce charcoal   A little before 1691 the Rev. Dr. John Clayton, Dean of Kildare, addressed a letter to the Hon'ble Robert Boyle, in which he described an experiment on the production and storage of inflammable gas, distilled from coal. This letter was published in the Royal Society's Transactions in 1781. In 1783 Prof. Jan Pieter Minckelers of Louvain made coal gas and used it the same year for ballooning, and in 1785 and in succeeding years, he used coal gas, purified by lime, for lighting his class room. In 1787, Lord Dundonald made some domestic experiments on lighting by coal gas, but it was not till 1792, exactly a century from the time of John Clayton, that William Murdoch lit up his house and office at Redruth in Cornwall with coal gas. In 1798, he lit up a part of Boulton and Watt's manufactory at Soho in Birmingham, and in 1805 he installed a thousand gas burners at the mills of Messrs Philips and Lee at Salford. It was thus that the attention of the world was drawn to the suitability of coal gas for general heating and lighting purposes. Till then, coal was nothing more than a fossil useful only for burning on domestic gratings and for firing boilers. Soon, metallurgy demanded its share, and coal became an industrial product of considerable value, and the method of its processing began to attract the attention of scientific workers.   The practice of coal carbonisation is still in its infancy in India, but in more industrially developed countries it has gone several stages further. Coal is now not only yielding tar and gases on distillation but the coke, under the action of air and steam, is being completely converted into combustible gases, far more suitable and economical for industrial operations than the solid coal itself.

The history of the later processing of coal is one of how efficiently it could be converted into gaseous and liquid products to adapt them not only to the heat requirements of industrial and domestic operations but also to internal combustion engines. The present position of the heat treatment of coal can be summed up by saying that on the one hand, complete success has been attained in the liquefaction of coal through reaction with hydrogen under pressure and heat, and on the other hand, the same end has been attained through an intermediate stage of complete gasification and the conversion of the gases into liquid fuels. Between these two ranges lie the three types of coal carbonisation that are in vogue today. All these three have for their objective the respective needs of the industries,—coke, gas or tar. The automotive industry has, however, claimed its source of propulsion from liquid fuels mainly, and in countries, where petroleum is insufficient but coal is in plenty, the tendency has been to extract as much liquid fuels from coal as possible, by the simple process of distillation, and when still inadequate, complete liquefaction of coal by complex processes has been attempted. The world consumption of synthetic motor fuels from all processes rose from 2·39 million tons in 1936 to 2·83 million tons in 1937, an increase of 0·44 million of tons. The increase in Germany alone was 0·465 million, so that in the rest of the world, consumption fell mainly owing to the production and use of 0·15 million tons of alcohol in France. The production of benzole has increased steadily, the world output rising from 1·14 million tons in 1936 to 1·27 million tons in 1937. In Great Britain, the production of motor benzole rose to 56 million gallons in 1937, an increase of 10% over the previous year. The output of refined motor spirit from low temperature carbonisation also increased from 0·8 million gallons in 1936 to 1 million gallons in 1937. The activities in this direction in Germany are more noticeable and instructive from the Indian point of view, for both countries lack coal and good coal. Germany showed a large increase in benzole production by 14%, that is, 430,000 tons in 1937 as compared with 378,000 in 1936. The output of oil by the hydrogenation process has also continued to rise. In Great Britain, the Imperial Chemical Industries manufactured 35 million gallons of petrol in 1937 as compared with 33 million gallons in 1936. In the output for 1937, 2 million gallons of aviation spirit are included. The production of synthetic gasolene by hydrogenation process in Germany rose to 850,000 tons in 1937 against 350,000 tons in 1936. Similar operations are noticed in France but on a very much smaller scale and in Japan a hydrogenation plant with an annual capacity of 20,000 tons is reported to be completed, whilst the South Manchurian Railway Co. intends to construct a

plant of 200,000 tons capacity. Italy and Russia are also erecting plants for the hydrogenation of coal, and active researches are in progress on the hydrogenation of tars and oils.

It may be mentioned in this connection that the use of compressed gases as motor fuel is already attracting attention and producer gas generated *in situ* in lorries and tractors has met with a fair amount of use in western countries, specially in Germany, and less in France, England, Italy and Russia. In the U.S.S.R. gas producer marine motors are also stated to have given satisfactory results in service and Japan is proposing to use producer gas for buses in the near future. The recent use of anthracite in portable producers in motor cars, in England, is a further interesting development in the automotive industry. A cwt. of anthracite burnt in a producer is reported to be able to drive a 10 H.P. car over a distance of 100 miles at 50 miles per hour. Assuming 25 miles per gallon of petrol, this quantity of anthracite would be equivalent to 4 gallons of petrol, but the price differential between the two fuels is enormous. The refilling of the producer tank every 100 miles is easy, only the anthracite must be lighted before starting. The replacement of anthracite by soft coke or indeed by hard coke would introduce an economy in our petrol reserve, which, by no means, is large. All these represent a lesson to India which is now on the threshold of industrial development.

In India, of the 23 million tons of coal raised annually, about 3 million tons are used for making hard coke, whilst a little more than a similar quantity is used for domestic purposes where much valuable combustible products are lost. Barring the 3 million tons of coal, processed for metallurgical or foundry coke, the remaining 20 million tons could be utilised for all other purposes in the form of what is technically known as soft coke. By the introduction of a further process, *i.e.*, the Mond gasification of this coke, ammonia equivalent to 80-90 lb. of sulphate could be recovered per ton of coal handled. The low and medium temperature carbonisations are both suitable for producing the soft coke which renders all firings smokeless into the bargain. Besides, the possibility of converting low grade coals into better types of soft coke by blending, is admittedly a great point in favour of low temperature carbonisation, as high grade coal exists in very limited quantities in India. The by-products of low temperature carbonisation are larger quantities of tar (15-18 gallons) than by the high temperature distillation, and smaller outturn of gas (3-4 thousand c. ft.) of higher calorific value, per ton of coal. Both the tar and the gases by low temperature carbonisation have different chemical compositions

from those by the high temperature, but their applicability is not impaired in any way and they are more suitable for specific purposes. Whilst the demand for metallurgical coke puts a restriction to the quantity of coal that could be subjected to high temperature° distillation, soft coke could replace coal in all other operations, industrial or domestic. Recent researches by the speaker and his collaborators have given indication that an ' after-coking ' of the soft coke produces a substantially hard coke, the use of which in foundry and metallurgical operations is visualised. With a fuller development of this aspect of the question, it would appear that modern high temperature coking may have to be preceded by low temperature carbonisation as a general practice. There are certain obvious difficulties, both technical and theoretical, in the practical carrying out of this combined process, but a plant devised by the speaker and his collaborators, Roy and Ghosh, which will be described later (vide infra), has given promising results in this direction. In France, the medium temperature coking process has established itself firmly, and several big plants are in operation. As a matter of fact, the poor anthracite deposit in France has led her to medium temperature carbonisation of coal, which, after preliminary treatment, is eminently suitable for providing a substitute for anthracite. Considering the Indian situation, therefore, it would appear that low temperature carbonisation followed by hard coking has an unlimited scope as compared with merely high temperature coking. It has been contended that low temperature carbonisation is uneconomical and that the cost of plants is prohibitive. Its slow development in England (where the conditions are totally different) has been regarded as proof positive of the uneconomical nature of the process itself. But the fact that the Coalite plants are now carbonising at least half a million tons of coal annually, and that the Government of the U. K. have encouraged the establishment in Wales of a similar plant for treating 180,000 tons of coal annually, leaves no doubt that low temperature carbonisation of coal is no longer in the experimental stage. Besides, a difference in the prices of coal at the mouth of the pit in India and in England must be regarded as a better guarantee for such projects in this country. Then again, there is at present in India a definite market to the tune of one million tons for soft coke which is on the increase. In Germany, where the low temperature distillation of brown coal has been practised for years, several low temperature carbonisation plants for steam coal also exist, whilst many more have been built ready for operation. One might generalise that in countries, where both coal and petroleum are in abundance, the development of coal carbonisation for obtaining liquid fuels would naturally be slow. The United States of America could be cited as an

instance to the point. For India, as already indicated, low temperature carbonisation has a special significance, although against the immediate possibilities of low temperature carbonisation, the absence of suitable markets for the by-products of the industry, has been cited as a ground. The rapid increase in the liquid fuel consumption in this country for auto motive and stationary internal combustion purposes, coupled with the low petroleum deposit, is alone a guarantee for the complete utilisation of the liquid products of coal carbonisation. As a matter of fact, petroleum and low temperature liquid fuels in India might be regarded as complementary without bringing unhealthy competition. The low temperature pitch after aeration is suitable for road surfacing, and its use in baking enamel varnish would provide a considerable outlet. The carbolic fraction of the tar, often amounting to 10-20% of the volume has its definite uses, and any excess can under slightly altered technique be used for internal combustion engines, plastic industry, and as disinfectants.

The technique of low temperature carbonisation has developed through many stages of failure. The main features of a workable plant are (i) control of temperature of distillation, (ii) rapid conduction of heat through the mass of coal, (iii) discharge of the coke in the form of pieces of suitable size, with a minimum of breeze, and (iv) the maximum life of the retorts. With the above four criteria in view, attempts have been made again and again in all parts of the world to devise the most suitable plants and processes often differing from one another only in details and not essentially in principle. A brief survey of the situation in 1938 would be as below :

In January, 1938, 736 brown coal carbonisation plants were in actual operation in Germany, distributed as under :

Rolle ovens	588
Carbonisation ovens according to Geissen-Kohlenveredlung	35
Gas Producer with low temperature coke production	38
Internally heated ovens by the Lurgi system	62
Carbonisation ovens of Borsig-Geissen type	5
Internally heated ovens of different designs	8

With regard to low temperature steam coal carbonisation, no less than 15 plants were in operation in 1938, to which must be added a few where the carbonisation is carried out at the medium temperature of about 700°C. The more important processes for low temperature carbonisation are :

A. Externally heated :

1. The Coalite Process in England.
2. Brennstoff-Technic Process in Germany.
4. Puening oven in England
3. Krupp-Lurgi Process.
5. Berg & Co's Process.

6. Hinselmann Process.
7. Otto Process.
8. Plate oven of Ab-der-Halden.
9. Process of Compagnie Generale Industrielle Carmaux.

B. Internally gas heated:

1. Lurgi Gesellschaft oven
2. Kollergas-Gesellschaft Process.
3. Delkeskamp Process.

4. Coalene-superheated steam Process.
5. Maclaurin Process.
6. Kivioli-Lurgi Tunnel oven.

C. Electrically heated shaft oven (internal)..

Of the medium temperature distillation plants, mention may be made of the following :

1. Koppers Process.
2. Otto Process
3. Cellan-Jones oven

4. Lecocq Process.
5. Kemp oven.
6. Roser Process.

A most important development in the low temperature carbonisation process has been the carbonisation of oil-coal mixtures, leading to considerable increase in the tar oil yield. Mention may be made of the rotary oven of Salerni, Brassert-Knowles Process, the Corby Process, Curran-Knowles oven, Blummer Process, Process of the Coal and Allied Industries, Ltd., Process of Messrs The Catalysts' Ltd., National Coke and Oil Co. Ltd., and the Hampton-Ryan Process of America. All these processes were and are still under trial, and their capacities limited to below commercial quantities in some cases.

An application of the carbonisation process for boiler-firing deserves also special mention, as its adoption is a factor of great technical importance. Of the various processes, the name of the Pintsch process easily stands first, but those of Berg, Babcock, Hereng and Stanley Morgan cannot be passed over.

It is beyond the scope of this paper to go into the merits of each of the systems most of which are characterised by one special feature or another. Whilst in general the problem of rapid heat transference to the coal is the main objective, and the refinements relate principally to this, giving rise to movable parts in the carbonising retorts, the ejection of the coke in a form

suitable for domestic use without briquetting has brought round designers oft and again to stationary retorts.

Briefly reviewing the characteristics of the different processes, certain generalisations could be formulated. It is obvious that plant, design and plant durability will depend upon the method of heating, whilst the nature and the amount of by-products will depend in no small a measure on this factor as well. Internal heating will lead to considerable fuel economy, but also to dilution of the gases, and even partial oxidation of the products of distillation. The structural material for the internally heated retorts can be firebrick, capable of withstanding the usual temperature of carbonisation without much deterioration. Besides, the heating gases being in direct contact with the mass of coal, both uniformity and rapidity of carbonisation can be secured. Thus, the quantity of coal that can be handled is very much more than by the externally heated system of retorts, which must of necessity be of cast iron or cast steel. It would appear, therefore, that internally heated chambers or shafts would provide the most ideal plant, the resulting gases being, however, very dilute and, with easily caking coals, the fire gases cannot uniformly pass out through the mass of coal. The dilute gases necessitate the use of large regenerators or recuperators to attain the proper temperature of firing, and having to deal with large volumes of gas, the plant for condensation of the volatile products is larger and the power for working the burners greater. Modern practice has, therefore, progressed in both the directions of internal and external heating, whether the coke discharged is intermittent or continuous. The externally heated retorts are more compact and simpler, and the volatile oils are definitely more in yield. With a proper choice of the thickness of the coal layer to be distilled and simple but efficient means of stirring, the outturn of coal carbonised can be very considerably increased. It can be shown from theoretical considerations that the time, M, required for carbonisation is related to the thickness, R, of the coal layer which must be penetrated by the heat, by the following equation :—

$$M = K(R + C)^2$$

where C is a small constant depending on the nature of the coal. Working at 713°C with a Pittsburgh seam coal in a 6·28″ radius retort, the actual time of carbonisation was 335 minutes or approximately $5\frac{1}{2}$ hours (Allison, *Ind. Eng. Chem.*, 1930, **22**, 841). The appropriate reduction in the thickness of coal layer will, therefore, achieve faster carbonisation even in stationary charges, and by introducing slow raking or stirring, this speed can

be very much more accelerated. Early in 1937, Sen and Roy (*Proc. Inst. Chem. India*, 1937, 21) designed a technical retort combining the implications of this equation, and a system of external and internal heating at will, increasing the elasticity of operation thereby. It has been possible by this combination to carbonise 8 lbs. of coal per square foot of hot surface per hour, with a heat consumption of 11 − 12% on the weight of the coal carbonised. As the plant in its simplified form has been tried in two instances with satisfactory results, its working deserves further consideration in view of the oft-repeated drawback in the form of costliness attributed to low temperature carbonisation plants. In designing a technical unit for operation in a country like India at the present state of meagre industrial development, it has to be recognised that capital is shy for new ventures and that the first desiderata of a low temperature carbonisation plant should be its simplicity of operation, cheap construction and introduction of mechanical devices only to an extent that does not substantially reduce the scope for manual labour. The technical plant designed can carbonise 50-60 tons of coal per 24 hours when provided with stirrers, but 36 tons when the coal is stationary and the withdrawal of coke intermittent. The plant consists of an assemblage of several sections of three concentric cast iron cylinders (A, B, and C) having diameters 10′, 7′ and 3′ respectively, and height 3′3″ each. These cylinders when they rest on the base plate (D), form three concentric compartments (E, F and G), of which the central (G) and the outermost (E) serve as the coal packing chambers and the annular space (F) in between the cylinders (B and C) is provided with a grating (H) and is used for firing coke to supply the heat. The coal containing compartments (E) and (G) are provided with removable doors at the bottom (I), which can be kept in position or detached, by proper lever arrangements (J). Each cast iron cylinder is provided with a deep circular groove (K) at the top into which another set of three concentric cylinders can fit properly. In this way by placing four such sets of concentric cylinders, one above the other, the proper coal-carbonising retort has been built up with an approximate height of 12′ 6″. The grooves are all secured gas-tight by fire-resistant cements. The outermost cylinder (A) in each set is provided with a delivery pipe (L) for the escape of the products of distillation. The inner coal chamber (G) is also connected with the outer coal chamber by suitable pipe connections (M_1), so that the products of distillation from the inner coal chamber can enter into the outer and then escape through the delivery pipes (L, L, L, L). These four delivery pipes are separately connected to condensers (M, M, M, M) and the condensed liquids from each of the four condensers collect in separate tanks (I, II, III, IV). The tank (I) which

is connected with the top-most condenser collects oil, mixed with a large quantity of water, whilst the other tanks collect oils with very little water. The reason is obvious, because in the continuous process, while descending from the top, coal loses most of its moisture and consequently the delivery pipes at lower heights discharge volatile products with only the steam of decomposition, and so the tanks which are in connection with these pipes through the condensers collect mainly oils with diminished quantities of water. The gases that escape through the condensers still contain sufficient low-boiling constituents (benzines, benzols, etc.) and, therefore, they are led into a tower (N) provided with a large number of partitions or packed with coke, upon which creosote oil continuously trickles from a reservoir (W) at the top. These fine drops of creosote oil absorb most of the light oils in the gases and ultimately collect in the tank (V) below. This oil is again pumped up to the top and the cycle is repeated. The lighter oils are separated from the creosote oil by simple distillation and the residual oil is again used as an absorbent (*vide* Fig. 1).

There are hoppers (P, P, etc.) at the top through which coal and coke could be charged at intervals. There are also arrangements for internally heating the semi-coke by hot flue gases from the combustion and coal chambers to improve the quality of coke and render it hard, if so desired. As a matter of fact, all the cylinders can be used as coking chambers of the internally heated type.

The wall thickness of the cast iron cylinders is 1″ throughout, but the bottom section is thicker. There are thick vertical ribs in different segments, which impart sufficient strength to withstand heavy weights and maintain their shape at high temperatures. There are also angle iron bars fastened to these ribs to give additional strength to the retorts. There are arrangements for hanging sheets of iron plates in the coal-containing chambers (E and G) from the top for facilitating better conduction of heat into the coal layers (not shown in figure). Provision is also made for the introduction of gas, air and steam through the set of three holes (S, S, etc.) at different points of the cylinders. Arrangements for continuous loading and discharging could be adopted by the introduction of helical conveyers as shown in one of the cylinders. Numerous doors at each section permit of short-length poking and consequent easy discharge of coke.

General Considerations in a Technical Unit.

It would be important at this stage to examine the probable cost of a commercial unit of this type of coking plant treating, say, 15 tons per 10 hours, intermittently, or 60 tons per 24 hours of continuous operation.

2

For the present, an intermittent system will be considered, although, there is no inherent difficulty in operating the plant continuously, which would also reduce the fuel and other costs.   The 15 ton plant would require 500 c. ft. of fire-brick work to enclose the cylindrical cast iron retorts, the latter roughly weighing 250 maunds (approximately 9· tons). To this must also be added the platforms and hoisting arrangements for the coal to be introduced into cylindrical retort spaces.   The hoisting of 15 tons of coal and the other mechanical devices, would not consume more than 3 H. P. H.

		Rs.
500 C. ft. of fire-brick @ Rs 200 per 100 c. ft		1000
250 Maunds of cast material @ Rs. 8 per md.		2000
Chimney and platform		2000
Constructional charges		1000
Shed (corrugated) over the unit		1000
Cost of fraction of power plant including boiler and air compressor ...		2000
Cost of a fraction of workshop		1000
Condenser and tar rectifier		5000
		15,000

It is obvious that the last three items have been liberally allowed for to avoid any unforeseen expenses.   We can now proceed to formulate a balance sheet for coking coal at Rs. 2 per ton at the pithead.

Cost of coal.

15 Tons of coal at Rs. 2 per ton   ·   ...   .   Rs. 30

Cost of carbonising.

	Rs. As. P.
(*a*) Cost of fuel at 11% of the weight of the coal 3 5 0	
(*b*) 5 Ordinary labourers @ 5½ as. a day ... 1 11 6	
(*c*) ½ of a shift Engineer or mechanic 1 0 0	
(*d*) ½ of a Chemical Engineers's wages 2 0 0	
Interest on Rs. 15,000 @ 5% 2 1 0	
Depreciation at 10% on Rs. 15,000 ... ... 4 2 0	
Overhead charges including power required 2 0 0	
Total cost 46 3 6	

Proceeds.

<div style="text-align:right">Rs. As. P.</div>

11·25 Tons of soft coke @ Rs. 2-12 per ton	... 31	0 0
154 Gallons of distilled tar fractions	... 35	15 6
Gas (90,000 c. ft.) as proportionate reduction of fuel cost ...	... 3	5 0
Pitch 3 cwt. @ Rs. 1-4 per cwt	... 3	12 0

<div style="text-align:right">74 0 6</div>

Net profit on Rs. 15,000 is, therefore, 74/0/6−46/3/6=27/13/0, which works out at about 66 per cent. Even if the profits were reduced to half, low temperature carbonisat on is financially sound.

Two small plants are at present working with retorts of simplified design after the semi-large scale plant described herein. The one supplies gas to the laboratories of the Indian Lac Research Institute, which can treat 5 cwt. of coal per charge of 8 hours (see Fig. 2). This laboratory which was using the Mansfield cracking plant for 10 years, has adopted the small-scale simplified plant for the last 3½ years, working almost every day, and producing gas at a very much cheaper cost. The second plant which approximates more to the design of the semi-large scale plant, was inaugurated by the Bihar Government last year to investigate the possibilities of low temperature carbonisation of Bihar coals. This pilot plant can handle 1 ton of coal per 24 hours of semi-continuous operation. Below are given comparative working sheets for the usual stack-burning method of soft coke production, for the Bihar Government pilot plant and for the tentative plant (yields for which are based on the Namkum plant) described above as a basis for future commercial venture. In Table II are also given figures for actual yields obtained by Messrs The Low Temperature Carbonisation Ltd., London, for samples of Indian coal.

<div style="text-align:center">TABLE I.</div>

		Open burning method for 15 tons.	Sen and Roy 15 ton plant per 10 hours.	Bihar Government Pilot plant: (1 ton per 24 hrs.).
Cost of plant :	Nil		Rs. 15,000 (approx.).	Rs. 1,500 (actual).
Analysis of coal used :	Fixed carbon	52·29	52·29	52·09 *
	Volatile matter	26·59	26·59	21·61
	Ash	19·62	19·62	26·15
	Moisture	1·50	1·50	0·82
Yields :	Coke	10 tons	11·25 tons	17·25 cwt.
	Crude tar	nil	195 gals.	8·5 gals.
	Distilled tar	nil	154 ,,	5·6 ,,
	Gas	nil	90,000 c.ft.	5500 c.ft.
	Pitch	nil	3-4 cwt.	26 lbs.

<div style="text-align:center">* Lower and Upper Jharia Colliery, Seam No. 10.</div>

	Open burning method for 15 tons.	Sen and Roy 15 ton plant per 10 hours.	Bihar Government Pilot plant (1 ton per 24 hrs.).

Cost sheet : 15 Tons of coal @ Rs. 2 per ton: Rs. 30

Cost of coal   Rs. 30
Cost of fuel at 11% of the weight of coal   Rs. 3-5

Cost of coal   Rs. 2
Cost of fuel at 18 % of the weight of coal   Rs. 0-5-9

Labour charges @ -2- per ton of coke
       Rs. 1-4-0
       Rs. 31-4-0

5 Coolies @ -5-6 a day   Rs. 1-11-6
½ of Shift Engineer or Mechanic   Re. 1-0
⅓ of Chemical Engineer   Rs. 2-

4 Coolies @   -5-6 a day   Rs. 1-6
Supervision   Rs. 8

Cost of 1 ton of soft coke   Rs. 3-2-0

Depreciation @ 10 % on Rs. 15,000   Rs. 4-2

Depreciation @ 10 %   As. -8-

If the selling price of soft coke at colliery be taken at Rs. 2-12- as stated by the Soft Coke Cess Committee two years ago, evidently the price of coal used by stack burners must have been between Re. 1-8- and 1-10- per ton. Corresponding changes in the price of coal under retorting conditions would show very much ,more profits.

Interest on Rs. 15,000 @ 5% per annum   Rs. 2-1
Overhead charges including power   Rs. 2
       Rs. 46-3-6

Interest @ 5%   -4-
Overhead charges As. -2-
       Rs. 12-9-9**

Proceeds :

Coke 11·25 tons @ Rs. 2-12 per ton   Rs. 31
154 Gals. of distilled tar fractions (a) Light oil 18 gals. @ -6- Rs. 6-12

(a) Coke 17·25 cwt. @2-12   Rs. 2-6
(Distilled tar 5·6 gals from 8·5 gals. of anhydrous crude tar)

(b) Middle oil 47 gals @ -4•   Rs. 11-12

(b) Light oil 0·79 gals. @ -6- As. -4-8

10 Tons coke @ Rs. 2-12 Rs. 27-8

(c) Heavy oil 25 gals. @ -3-6   Rs 5-7-6

(c) Middle oil 2 gals. @ -4-   As. -8-

(d) Anthracene oil 64 gals. @ -3- Rs. 12

(d) Heavy oil 2·82 gals. @ -3-6   As. -9-10-

(e) Pitch 3 cwts. @ 1-4-0   Rs. 3-12-

(e) Gas at the price of fuel used   -5-9

(f) Gas at the price of fuel used   Rs. 3-5-0
       Rs. 74-0-6

(f) Pitch 26 lbs.   -5-0
       Rs. 4-7-3

** Deducting the sale proceeds from Rs. 12-9-9, the *actual* experimental cost per ton of coal carbonised, there is an adverse balance of Rs. 8-2-6. Of this, Rs. 8 are the salary of two research workers on the pilot plant. A technical plant for treating 15 tons of coal per 10 hours would require coolie labour to the tune of Rs 1-11-6, and supervision charges of Rs 3 only (*vide supra*). In other words, a sum of Rs 4-11-6 divided by 15, *i.e.*, about 5 annas would have been the labour and supervision charges as against the actual figure of Rs. 9-6. Introducing this correction in the actual working sheet of the Bihar Government Pilot Plant, the carbonisation costs including coal would have been Rs. 12-9-9 *minus* Rs. 9-1-0 or Rs. 3-8-9 Or, a profit of Rs. 4-7-3 *minus* Rs. 3-8-9 or Rs. 0-14-6 would accrue per ton of coal handled, which is very much more than could be expected from ordinary stack-burning.

TABLE II.

Analysis of certain Indian coals and yields of products therefrom.

	1.	2.	3.
Fixed carbon	52·29	62·13	61·44
Volatile matter	26·59	28·01	27·64
Ash	19·62	8·48	9·52
Sulphur	0·85	0·60	0·50
Moisture	1·50	1·38	1·40
Coke	16·50 cwt.	16·50 cwt.	16·36 cwt.
Oil	15·28 gals.	16·01 gals	14·22 gals.
Gas	2495 c. ft. = 18·34 therms.	2688 c. ft. = 18·98 therms.	2627 c. ft. 20·07 therms.
Liquor	11·11 gals.	11·11 gals.	12·63 gals.

The question of fuel economy in the distillation of coal has been discussed from so many points of view in the past and the economy has been effected to such a fine degree that this does not constitute the main problem of low temperature carbonisation to any essential extent. More refinements are possible, say, by the introduction of.Bone's flameless combustion. But the real point is the difficult penetration of heat through layers of coal, specially, when the latter is in its plastic condition during the early stage of distillation. This has necessitated the maintenance of comparatively thin layers of coal in the design of most retorts. But the design of coking ovens is to a large extent bound up with the size of coke desired in the end, specially where no. subsequent briquetting is contemplated. Up to a width of 9-11″ the coking may be considered complete in 5½ hours but if the coal layer is more in thickness, direct or internal heating is unavoidable, if stirring is not resorted to. One has to choose between mechanical stirring and internal heating, according to the size of the coke desired. In the 15-ton unit, 18″ annular space for the outer cylinder does not appear to be excessive in view of the fact that both surfaces of this annular are constantly receiving heat. Besides, it is possible to divert a part of the gas from the inner retort to the outer one for heating by its sensible heat or by the heat of combustion with a limited supply of a r ·
The chief feature of the process, however, is the provision of a larger heating surface, as much as one square foot per 8 lbs. of coal per hour as against the usual practice of 15 lbs per square foot per hour. This would considerably overcome uneven coking, specially, if the annular fuel space is used as a producer and the combustible gases produced here are burnt around or allowed to circulate through the outer cylindrical retort before entering the chimney.

It would further be noticed that no ammonia recovery plant has been taken into consideration, for the simple reason that it would not pay smaller carbonisation plants to recover the much smaller amount of ammonia in the distillation liquor and the gas. Low temperature carbonisation of coal yields 5 to 10 lbs. of ammonium sulphate per ton of coal carbonised. Roy, De and Guha (*J. Indian Chem. Soc. Ind. News Ed.*, 1938, **1**, 48) have in their most important investigation on Indian coals studied this point exhaustively in the case of some of the important Bengal coals. Coals with high volatiles yield higher quantity of ammonia, but this is by no means general. From the by-product point of view, coal under 20% volatiles is practically useless, both as regards tar and ammonia yields. The medium temperature carbonisation raises the yield of ammonium sulphate to 20-22 lbs. per ton of coal, but there is a definite fall in the tar yield and change in the characteristics of the tar oils, *e.g.*, in the phenol-neutral oil ratio, and yield of anthracenes.

Thus the specific requirements of the industry should determine the type of carbonisation, and the recovery of by-products would constitute an essential economy. If soft coke, *i.e.*, smokeless fuel is the object, the recovery of ammonia is not so important as the processing of the tar. But if power production by steam turbines is the goal, a combination of low temperature carbonisation with subsequent Mond gasification of the soft coke would appear to be the most rational way of coal treatment. In this combined scheme, both the tar oils as also the highest quantity of ammonia are realised. The background of soft soke as a rational fuel remains as sound as ever, as power producers could make soft coke the starting point for Mond gasification and recover as by-product this extraordinarily high quantity of ammonia. From a critical examination of this process of heating gas production, it could be shown that at the mouth of the pit, electric power could be generated at as low a figure as 0·082 annas or 0·984 pies per unit.

Low temperature carbonisation plants have been quoted at from abroad between Rs. 1500 and 3500 per ton of coal carbonised per day. There is no doubt that by manufacturing the plants in India, a considerable saving on this head could be possible, ensuring thereby larger margin of profit. If the 1·2 million tons of coal that are annually coked to-day to produce about 800,000 tons of soft coke, were distilled in retorts with no more refinement than the collection and fractionation of the tar, we should be saving at least 10 × 1·2 = 12 million gallons of liquid fuel per year. Its general adoption as a measure for the rational treatment of coal would for many years place a source of liquid fuels and manure in our hands which we are at present losing through lack of ordinary organisation.

COMPONENT GLYCERIDES OF VEGETABLE FATTY OILS.
PART I.   NIGER SEED OIL.

By N. L. Vidyarthi and M. Venkatesh Mallya.

The fatty oil extracted from the seed of *Guizotia abyssinica* (Niger seed) has been found to contain myristic acid (along with some capric, caprylic and lauric acids) (1·7%), palmitic acid (5%), stearic acid (2%), oleic acid (38·9%) and linolic acid (51·6%) along with traces of archidic, behenic and lignoceric acids.

The glyceride structure of the oil has been determined by brominating the neutral oil, resolving the brominated solid and liquid products into a number of simpler fractions and estimation of the fatty acid composition of the different fractions. The component glycerides of the oil have been found to be trilinolin (2%), oleo-di-linolin, (40%). di-oleo-linolin (30%), myristo-di-linolin (2%) myristo-oleo-linolin (3%), palmito-di-linolin (6%), palmito-oleo-linolin (11%), stearo-di-linolin (2%) and stearo-oleo-linolin (4%).

The methods adopted by Hilditch *et al.* (*J. Soc. Chem. Ind.*, 1938, **57**, 44) for the determination of glyceride structure of solid seed fats cannot be adopted for the liquid fats, because they do not contain any appreciable quantity of di- or tri-saturated glycerides. Up till now there has been no satisfactory method for the study of the fully unsaturated glycerides. With a view to explore a satisfactory method for the quantitative estimation of the triolein in natural and synthetic fats, Hilditch and Griffith (*J. Chem. Soc.*, 1932, 2315) converted oleic acid into elaidic acid. But they found that only 66% of the acid could be converted to elaidic acid when the equilibrium was attained and the process could not be used for any quantitative work.

Hilditch and Jones (*J. Soc. Chem. Ind.*, 1934, **53**, 13T) examined the glyceride structure of a number of technically important fatty oils by the fractional crystallisation of the fully hydrogenated oils from different solvents. This method does not throw any light upon the association of the different unsaturated acids in the glycerides.

Suzuki and Yokoyama (*Proc. Imp. Acad. Tokyo*, 1927, **3**, 529) and Hashi (*J. Soc. Chem. Ind. Japan*, 1927, **30**, 849 ; 1928, **31**, 117) brominated a number of vegetable and fish oils and determined the glyceride composition of these oils by the fractional crystallisation of the solid bromo-glycerides from different solvents. They could not examine the liquid bromo-glycerides, which are the products of bromination of the glycerides containing mono- and diethylenic acids. Stein and Ulzer (*Chem Zentrl.*, 1928, **II**, 1337) and Sahashrabudhi and Kale (*J. Univ. Bombay*, 1932, **2**, 37) have brominated Niger seed oil and they have reported some qualitative results,

The present work has been taken up with a view to find out a method for the quantitative estimation of the component glycerides of the fatty oils, and it has been found that the quantity of fully unsaturated and di-unsaturated glycerides containing mono- and diethylenic acids can be determined from a fatty oil by resolving the liquid bromo-glycerides into a number of simpler fractions by extraction with different solvents. The method has been tried upon the Niger seed oil and a number of other vegetable fatty oils is being studied by this process. The method is described here in brief.

The component fatty acids of the oil are determined by the usual method of lead salt separation, ester fractionation and hexabromide estimation. Then the neutral oil is dissolved in 6 times its weight of dry acetone and crystallised at 0°. Any fully saturated or disaturated glyceride will crystallise out. The quantity of fully saturated glyceride in the oil is determined by successive oxidation of the neutral oil in acetone solution (Hilditch and Lea, *J. Chem. Soc.*, 1927, 3106). The neutral oil or the glyceride, from which fully saturated and disaturated glycerides have been separated out, is dissolved in low boiling petroleum ether and brominated at 0°. The solid and liquid bromo-glycerides are further resolved into a number of fractions with benzene, acetone, alcohol and acetone and alcohol mixture (1 : 1). All the fractions are debrominated, the component fatty acids are determined and the amount of the various glycerides in the fractions is calculated.

Niger seed oil has been found to consist of the following glycerides : Tri-linolin (2%), myristo-di-linolin (2%), myristo-oleo-linolin (3%), palmito-li-linolin (6%), stearo-di-linolin (2%), palmito-oleo-linolin (11%), stearo-oleo-linolin (4%), di oleo-linolin (30%) and oleo-di-linolin (40%). Palmito-glycerides contain the small quantity of lauric, and other lower acids and stearo-glycerides contain the archidic, lignoceric and behenic acids.

The neutral oil was hydrogenated in presence of nickel catalyst suspended on kieselguhr by agitation process to two stages, one to the iodine number of 1·8 and the other to the iodine number of 27·2. The former one gave 75·3% of tristearin on crystallisation from ether at 0° and the latter one gave 51·2% tristearin in 76·2% of fully saturated glycerides, on making allowance for the non-saponifiables of 2·4% in the oil. The amount of C_{18} glycerides calculated in the oil is about 77·3% and the remaining 20·8% of the glycerides contain at least one acid having less than 18 carbon atoms in the chain. It agrees fairly well with the results obtained from the brominated glycerides.

The oleic and linolic acids, being the major component acids, have distributed themselves evenly in the glycerides.

Experimental.

Finely crushed seeds of *Guizotia abyssinica* (Niger seed, N.O. 'Compositae*) were extracted with carbon tetrachloride. The oil, golden yellow in colour, was 40% on the weight of the seeds and had the following physical and chemical constants (*cf.* Crossby and Sueur, *J. Soc. Chem. Ind.*, 1898, 27, 991 ; Bolton, "Oils, Fats and Fatty Foods," p. 299).

Table I.

Sp. gr. at 28°	...	...	...	...	...	0·9475
Refractive Index at 25°	...	...	...	...	...	1·472
Sapon. value	...	...	...	...	...	189·7
Iodine value	...	...	...	...	...	129·2
Acetyl value	...	...	...	...	...	19·8
Free fatty acids (% as oleic acid)			...	...	...	4·27
Non-saponifiables	...	...	...	...	...	3·65%

Component Fatty Acids of the Oil.—440 G. of the oil were saponified and the non-saponifiables of the oil were extracted from the soap. The mixed acids, liberated from the soap, were subjected to the usual procedure of lead salt, alcohol and ether separation. The resulting acid fractions were converted into methyl esters and fractionally distilled under a pressure of 0·2 mm. as given in the following tables.

Table II.

	Wt.	Percentage.	Saponification equivalent.	Iodine value.
Oil	440 g.	...	295·5	129·2
Mixed acids (free from non-sap.)	403	91·7	281·5	129·4
(A) Acids from alcohol-soluble lead salts	233	57·5	281·3	1?·2
(E) Acids from ether-soluble lead salts	98·5	24·6	281·1	143·2
(S) Acids from insoluble lead salts	72·5	17·9	273·2	52·42
Esters of A			294·2	147·0
Esters of E			294·7	141·1
Esters of S			286·9	52·35

3

TABLE III.

Fractional distillation of esters A.

Stillhead.	Weight.	Saponification equivalent.	Iodine value.
60-120°	3·1 g.	186·6	54·68
120-135°	4·6	230·0	80·23
135-141°	6·8	287·0	124·8
141-145°	4·6.	292·4	147·9
—	4·5	295·4	155·1
145-150°	47·1	294·3	150·7
152-155°	32·0	294·3	157·6
155-160°	16·6	294·7	150·2
160-190°	7·8	294.6	120·4
—	24·8	309·1	121·0

, fraction A_6, contained 14% of non-saponifiables and the corrected
ᴛ.

TABLE IV.

Fractional distillation of ester E.

72-145°	5·3 g.	292·5	127·9
145-147°	3·0	292·6	142·2
147-152°	10·5	292·8	151·0
152°	6·2	296·8	138·5
—	12·4	295·8	139·0

TABLE V.

Fractionation of ester S.

90-140°	5·6 g.	262·3	25·2
140-142°	12·1	280·5	35·12
142-143°	12·0	282·6	55·82
146-150°	12·4	291·7	66·19
150°	3·5	291·7	49·74
—	7·9	307·1	49·60

Lauric acid (m.p. 42°), myristic acid (m.p. 52°), palmitic acid (m.p. 62°) and stearic acid (m.p. 62°) were identified from the various fractions by their mixed m.p. with authentic samples. By the oxidation of the fractions of the liquid acids in. alkaline permanganate (Lapworth and Mottram, *J. Chem. Soc.*, 1925, **127**, 1678), dihydroxystearic acid (m.p. 130°) and two tetrahydroxy acids, one melting at 154° and the other melting at 174°, were identified.

The residue S_6 from the solid esters gave three acids melting at 72-73°, 81-82°, and 75-76° having the saponification equivalents of 316·2, 342·2 and 366·6 respectively. The second one, melting at 81-82°, was identified to be behenic acid. The other two had lower melting point for straight chain archidic and lignoceric acids, though their equivalents are fairly correct. As these acids have been found to be present in vegetable fats in branched chain forms these have been considered to be branched chain archidic and ligno-ceric acids:
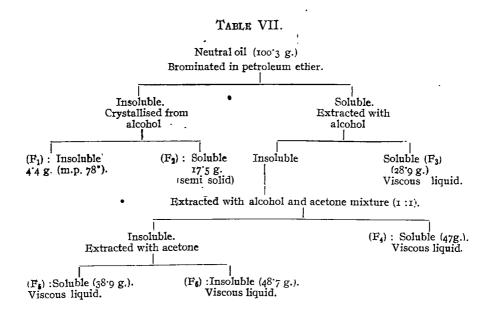
By steam distillation of the splitted up soap of the oil 0·7% of steam-volatile acids was obtained, which on estimation of barium from their barium salts were found to be a mixture of capric and caprylic acids. (Found : Ba, 62.8 and mean M. W., 163·1. Calc. for $C_{10}H_{20}O_2$: Ba, 54 per cent and $C_8H_{16}O_2$: Ba, 46 per cent. Equivalent, 162·1). On brominating the mixed acids of the freshly extracted oil ·in ether no hexabromide was obtained. Hence the oil does not contain any linolenic acid. From these observations the component fatty acids of the glyceride of Niger seed oil have been calculated as given in Table VI.

TABLE VI.

Acids.	In A.	In E.	In S.	% on mixed acids.	
				%by wt.	Mol. %.
	57·5%	24·6%	17·9%		
Lauric, capric, caprylic and myristic acids	0·8	nil	0·9	·1·7	1·9
Palmitic acid	0·3	—	4·7	• 5·0	5·6
Stearic acid	—	—	2·1	2·1	2·0
Archidic, behenic and ligno-ceric acids	—	—	0·2	0·2	trace
Oleic acid	20·5	8·9	10·0	38·9	38·9
Linolic acid	35·9	15·7	—	51·6	51·6

Component Glycerides.—The oil from Niger seed was rendered neutral by treating with sodium carbonate and filtered through decolourising charcoal.

The oil (101·2 g.) was dissolved in 600 c.c. of diy acetone and left overnight at o°. Nothing precipitated out and hence the oil does not contain any appreciable quantity of any disaturated glyceride. 490 C.c. more of acetone were added to the solution and it was oxidised thrice with powdered potassium permanganate. Finally it gave 1·2 g. of neutral product, which was found to be only non-saponifiables, and the oil was found to have no fully saturated glycerides.

The neutral oil (100·3 g.) was dissolved in one litre of petroleum ether and cooled down to −5°. Bromine was added slowly till the whole solution was permanently brown. It was left overnight at o°, the precipitate was filtered off and washed with chilled petroleum ether. It was further resolved into two fractions by crystallisation from alcohol. From the filtrate the excess of bromine was washed off with sodium thiosulphate solution and on evaporating off the solvent a viscous liquid was obtained. It was successively extracted with alcohol, alcohol and acetone mixture (1:1) and acetone. Four fractions, three soluble in the solvent and one residue were obtained. The general scheme of separation is shown in Table VII.

TABLE VII.

Neutral oil (100·3 g.)
Brominated in petroleum ether.

Insoluble.   Soluble.
Crystallised from   Extracted with
alcohol   alcohol

(F₁) : Insoluble   (F₂) : Soluble   Insoluble   Soluble (F₃)
4·4 g. (m.p. 78°).   17·5 g.   (28·9 g.)
                       (semi solid)   Viscous   liquid.

Extracted with alcohol and acetone mixture (1 :1).

Insoluble.   (F₄) : Soluble (47g.).
Extracted with acetone   Viscous liquid.

(F₅) :Soluble (38·9 g.).   (F₆) :Insoluble (48·7 g.).
Viscous liquid.   Viscous liquid.

All the fractions were debrominated by boiling with zinc dust and hydrogen chloride in methyl alcohol solution. The debrominated products

were saponified and acids were liberated after extracting the non-saponi-fiables. The quantity of individual acids was estimated in each fraction by determining their saponification equivalents, iodine values and thiocyanogen values. The quantity of saturated acids being too small in these fractions for estimating the amounts of individual acids, they were considered as one and their mean molecular weight was determined on extracting with petroleum ether the oxidation products of each fraction with alkaline potassium permanganate.

F_1 was obtained in a small quantity. Instead of subjecting it to the same procedure its bromine content was estimated according to the method of Bacons (*Chem. News*, 1903, 99, 6). It was found to be a triglyceride of tetrabromo-iinolic acid. (Found: Br, 52·02. Calc. for $C_{57}H_{98}O_6Br_{12}$: Br, 49.63 per cent). The analytical results are given in Table VIII.

TABLE VIII.

	F_1.	F_2.	F_3.	F_4.	F_5.	F_6
Weights (in g) ...	4·4	17·5	28·9	47·1	38·9	48·7
Saponification equivalent ...	—	276·7	278·2	282·0	281·7	281·9
Iodine value ...	—	121·6	92·7	121·7	147·4	147·6
Thiocyanogen value ...	—	61·3	59·0	90·1	90·0	90·1*
Weight of debrominated material (as glycerides and non-sap.) ...	2·1	10·0	17·5	26·4	44·8	
Weight of non-saponifiables ...	0·08	0·002	0·09	0·225	0·803	
% of glycerides (free from non-sap.)	2·0	10·0	17·4	26·2	44·4	
Saponification equivalents of the saturated acids	—	264·2	258·4	—	—	

* As the fractions 5 and 6 gave almost similar analytical figures, they were combined and considered as one fraction.

TABLE IX.

Mol. % of the acids in each fraction.

	F_1.	F_2.	F_3.	F_4.	F_5.	Mean.
Acids ...	2%	10%	17·4%	26·2%	44%	—
Saturated acids ...	—	32	33·5	—	—	9·2%
Oleic acid ...	—	2	30·4	65·6	37·4	39·1
Linolic acid ...	100	66	36·1	34·4	62·4	51·7

TABLE IX (contd.).

: acids in the fractions on total acids.

	F₁.	F₂.	F₃.	F₄.	F₅.	Mean.
...	—	3·3%	5·86%	—	—	9·16%
...	—	0·2	5·27	17·05%	16·6%	39·12
...	2·0%	6·5	5·27	9·15	27·8	51·72

ιin the experimental limits with the component
ιed from the oil direct.

he component glycerides of the Niger seed oil
ι in Table X.

TABLE X.

F₁.	F₂.	F₃.	F₄.	F₅.	Total in the oil.
2%	10%	17·4%	26·2%	44·4%	100%
Nil	Nil	Nil	Nil	Nil	Nil
—	—	—	—	—	—
—	9 3	1·5	—	—	10·8
—	0·6	15·9	—	—	16·5
—	—	—	25·1	5·4	30·5
—	—	—	1·1	39·0	40·1
2·0	0 1	—	—	—	2·1

he neutral oil with potassium permanganate in

he neutral oil from acetone at 0°.
ιt fatty acids of the brominated fractions.

ιve been considered as one acid in calculation of
.turated acids are combined in the glycerides of
ed-diunsaturated glycerides, the assumption that
ortionately divided in mono-saturated-dilinolin
n glycerides will not be incorrect. From the
:urated acids in the oil, the component glycerides
given in round figures as—trilinolin (2%),
olin (30%), myristo-dilinolin (2%), myristo-
inolin (6%),palmito-oleo-linolin (11%), stearo-

dilinolin (2%) and stearo-oleo-linolin (4%). The myristo-glycerides will contain small quantities of lauric, capric and caprylic acids which are about 2% and the stearo-glycerides will contain small quantity of archidic, behenic and lignoceric acids which will be less than 1%.

Glyceride Composition by the Progressive Hydrogenation of the Oil.— The neutral oil was hydrogenated in presence of nickel catalyst, suspended on kieselguhr by agitation at 140° till it was saturated (Iodine value 1·8). On crystallisation from ether at 0° it gave 75% of tristearin, melting at 71°, and had saponification equivalent of 297·6. Another portion of the oil was hydrogenated in the same way to an iodine value of 27·2. It gave 76% of fully saturated glyceride on successive oxidation with potassium permanganate in acetone. The fully saturated glyceride contained 2·4% of non-saponifiables. On crystallisation from ether the hydrogenated product gave 51·6% of tristearin. According to the observations of Hilditch and Bushell (*J. Chem. Soc.*, 1937, 1767) during the process of hydrogenation, the glycerides having one or more acids containing less than 18 carbon atoms are saturated before the glycerides containing acids with 18 or more than 18 carbon atoms. In accordance with this view the observation of the hydrogenated products of Niger seed oil shows that it must contain about 22·8% of the glycerides having at least one acid with less than 18 carbon atoms in the chain and the rest 77·2% of the glycerides must be only tri-C_{18} glycerides. This observation is in agreement with the glyceride composition obtained by bromination.

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THE FATTY OIL FROM THE SEEDS OF *BAUHINIA VARIEGATA*, LINN.

By S. V. Puntambekar and S. Krishna.

The oil from the seeds of *Bauhinia variegata* Linn, consists of the glycerides of myristic, palmitic, stearic, lignoceric, oleic and linoleic acids together with the phytosterol, sitosterol, commonly found in the vegetable fats.

Bauhinia variegata Linn, known as *Kachnar* in Hindi, is a moderate sized deciduous tree (N. O. *Leguminosæ*) of the sub-Himalayan tract from Indus eastward. It is often cultivated both as an ornamental tree and for its flowers which are eaten as vegetables. The pods are 6″-12″ by $\frac{3}{4}$″-1″ with 10-15 seeds which contain the fatty oil.

Fatty oils of the allied species *B. esculenta* (Bray, *Analyst*, 1921, **46**, 401) and *B. purpurea* (Kafuku and Hata, *J. Chem. Soc. Japan*, 1934, **55**, 369) were worked for their physical and chemical constants and *B. purpurea* oil was shown to consist of the glycerides of myristic, palmitic, stearic, archidic, oleic and linoleic acids. The constituents of the oil from the seeds of *B. variegata* are now reported for the first time

EXPERIMENTAL.

The seeds of *B. variegata* were collected locally at New Forest, Dehra Dun. They consisted of 20% of endocarp and 80% of kernel which yielded 16·5% of a pale yellow fatty oil when extracted with petroleum ether and 6·1% of it when expressed (hot expression) in a hydraulic press. The constants given below are for the sample of the oil obtained by hot expression.

Physical and Chemical Constants.

(The Fatty Oil).

Consistency	thin	Sap. value ...	211·0
Sp. gr. at 30° ...	0·9206	Acid value ...	2·8
Refrac. index at 30° ...	1·4603	Hehner value ...	92·0
Iodine value (Hanus) ...	91·3	Unsaponifiable matter ...	1·6%

Mixed acids.

Mean M.W.	... 294	Sat. acids	... 32·3%
Iodine value (Hanus)	... 93·2	Unsat. acids	... 67·7%

Composition of the Mixed Fatty Acids.

The oil (120 g.) was saponified in the usual manner with alcoholic sodium hydroxide. After distilling off alcohol the resultant soap was dissolved in water and the mixed acids liberated by the addition of strong hydrochloric acid. These were washed with warm water and neutralised with a 10% solution of sodium hydroxide. The soap solution was evaporated, incorporated with washed filter paper pulp and the resulting mass was dried, powdered and extracted with ether in a Soxhlet to remove the unsoponifiable matter. The mixed acids were liberated from the residual soap and purified in the usual manner.

The mixed acids (85 g.), free from the unsaponifiable matter, were separated into solid and liquid acids by Twitchell's lead salt method (*Ind. Eng. Chem.*, 1921, **13**, 806) and were found to possess the following constants.

Acids	Iodine value.	Mean M. W.	Net weight.
(S) Solid	2·55	272·2	27·5 g.
(L) Liquid	65·60	507·5	57·5 g.

The low iodine -value and the high mean M. W. were evidently due to polymerisation of the liquid acids as a result of their standing in contact with the laboratory atmosphere for some time.

Solid Acids (S).

The solid acids (27·2 g.) were dissolved in 200 c.c. of methyl alcohol containing 3·5% of dry hydrochloric acid and the solution refluxed for 5 hours. Methyl alcohol was distilled off and the resulting methyl esters were washed with saturated salt solution, water and 5% sodium carbonate and finally with water. After drying under vacuum, 27 g of the esters were distilled at 6 mm. into the following fractions,

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Fractions.	B.p.	Mean M.W. (of the acids)	Net wt.	Component methyl esters			
				Myristate.	Palmitate.	Stearate.	Lignocerate.
S₁	−172°	247·6	1·0 g.	0·8	0·2	—	—
S₂	172-75°	269·3	12·5	—	12·5	—	—
S₃	175-78°	287·0	3·5	—	1·4	2·1	—
S₄	178-82°	294·0	3·0	—	—	3·0	—
S₅	182-210°	296·0	6·0	—	—	6·0	—
Residue	—	—	0·8	—	—	—	0·8
Loss	—	—	0·2	—	—	—	—
Total	—	—	27·0	0·8	14·1	11·1	0·8
Per cent.	—	—	100·0	3	52·6	41·4	3

All these fractions were separately saponified and the corresponding acids were liberated and dried in the usual manner.

Acids from fraction S_1 on crystallisation from dilute acetone gave a product melting at 53°. Its mixed melting point with an authentic sample of myristic acid was 52-54°. From the mother-liquor on evaporation and drying a product (mean M. W. 259) was obtained. The fraction, therefore, appeared to be mostly myristic acid accompanied with some palmitic acid.

Acids from fraction S_2 on crystallising twice from dilute acetone gave a product, m.p. 62-63°, M.W. 258. Its mixed melting point with an authentic sample of palmitic acid remained unchanged. The mother-liquor on evaporation and drying yielded a product, M.W. 259. The fraction was thus almost entirely palmitic acid.

Acids from fraction S_3 on crystallising thrice from acetone gave crystals, m.p. 67-68°, M.W. 281. Their mixed melting point with a pure sample of stearic acid remained unchanged. From the mother-liquor a product (M.W. 260) was obtained. It thus appeared that the fraction consisted of palmitic and stearic acids.

Acids from fractions IV and V being similar (mean M.W. 280 and 282), were mixed together and crystallised twice from acetone giving crystals, m.p. 67-68°, M.W. 283. Their mixed melting point with an authentic sample of stearic acid did not show any change. The residue from the mother-liquor had a mean molecular weight of 285·6. The fractions thus entirely consisted of stearic acid.

Acids from the undistilled residual esters after three crystallisations from acetone gave a product, m.p. 75-76°, M.W. 369·2. Its mixed melting point with a sample of pure lignoceric acid showed no change. The acid was, therefore, lignoceric. The mother-liquor being highly coloured and the amount of dissolved acid being small, it was not examined further.

Liquid Acids.

Oxidation.—The liquid acids were saponified to break up any ethyl esters which might have been formed during the Twitchell's separation. A portion of the de-esterified acids was converted into potassium soaps and oxidised in cold alkaline solution with dilute potassium permanganate according to the modified method of Hazura (Lewkowitsch, " Chemical Technology and Analysis of Oils, Fats and Waxes," 6th Ed., Vol. I, p. 575). From the precipitated oxidised acids, dihydroxystearic acid, m.p. 131-32°, M.W. 315, and the tetrahydroxystearic acid, m.p. 155-56°, M.W. 350, were isolated and identified. The filtrate yielded azeleic acid, m.p. 101-2°, M.W. 186, and caproic acid, M.W. 116, indicating that the oxidation of oleic and linoleic acids present in the liquid acids had partly proceeded to rupturing the double bonds between the 9 and 10 carbon atoms in the case of oleic acid and the double bonds between the 9 and 10 and 12-13 carbon atoms in the case of linoleic acid.

Bromination.—Freshly prepared mixed acids (1·6581 g.) were brominated, according to the method of Eibner and Muggenthaler (Lewkowitschl, *loc. cit.*, p. 585) yielding 2·5441 g. of the brominated product (theoretical yield 2·6375 g.) but no hexa- or higher bromides. Crystallised from petroleum ether the brominated product gave white needles (m.p. 113-14°, M.W, 595) which were evidently those of tetrabromostearic acid, m.p. 113-14°, M.W. 600. This was confirmed by the mixed melting point with a sample of pure tetrabromostearic acid from other sources. The oxidation and bromination results thus clearly showed that the liquid acids consisted of only oleic and linoleic acids.

The above data on calculation gave the percentage of the constituent acids as follows :—myristic (1%), palmitic (17%), stearic (13·4%), lignoceric (1%), oleic (31·8%), and linoleic (35·9%).

Unsaponifiable Matter.

The unsaponifiable matter, obtained from the sodium soaps of the mixed acids by extraction with ethyl ether, when crystallised from 95 %

alcohol gave white plates, m.p. 125-26°, which on recrystallisation from the same solvent melted at 131-32° (acetate, m.p. 124-25°). The mother-liquor on concentration yielded plates, m.p. 125-26° (acetate, m.p. 124-25°). The unsaponifiable matter thus appeared to contain the common phytosterol, sitosterol, found in many vegetable fats. The residue burnt with a smoky flame and was insoluble in concentrated sulphuric acid and, therefore, appeared to consist mostly of hydrocarbons. The quantity was, however, small for further examination.

STUDIES IN DEHYDROGENATION. PART V.

*By Suresh Chandra Sen-Gupta.

The syntheses and selenium dehydrogenation of tetrahydrophenanthrene-2 : 2-spiro-cyclopentane and 9-methyltetrahydrophenanthrene-2 · 2-spiro-cyclopentane have been described The former on dehydrogenation gives chrysene and the latter forms 3-methyl 1 : 2-benzanthracene

In a previous paper (*J. Indian Chem. Soc.*, 1939, **16**, 349) an explanation of the mechanism of ring transformation of cyclopentane-spiro-hydrocarbons, during selenium dehydrogenation, had been offered. The results now obtained by the dehydrogenation of tetrahydrophenanthrene-2 : 2-spiro-cyclo-pentane (V, R=H) and 9-methyltetrahydrophenanthrene-2 : 2-spiro-cyclo-pentane (V, R=Me) go to support the former view.

The spiro-hydrocarbon (V, R=H) has been synthesised readily by the following steps. The anhydride of cyclopentane-1-carboxy-1-acetic acid condenses with naphthalene in presence of anhydrous aluminium chloride giving a mixture of two isomeric keto-acids. They are separated by fractional crystallisation and purified through the methyl ester. The lower melting keto-acid gives α-naphthoic acid on oxidation with sodium hypobromite and, therefore, it is αα-cyclopentane-β-1-naphthoylpropionic acid (I, R=H),

(I)

(II)

(III)

whereas β-naphthoic acid is obtained from the less fusible one, which is, therefore, the β-2-naphthoyl acid (II). The position of the *cyclo*pentane ring has been assumed from an analogy with the constitution of the keto-acids obtained by the condensation of the anhydride of *cyclo*pentane-1-carboxy-1-acetic acid with benzene and its homologues (*loc. cit.* p. 350). The keto-acid (I, R=H) on reduction by the Clemmensen method gives $\alpha\alpha$-*cyclo*pentane-γ-1-naphthylbutyric acid (III, R=H), which is cyclised with 85% sulphuric acid to 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene-2 : 2-spiro-*cyclo*pentane (IV, R=H). This spiro-keto compound on reduction by the Clemmensen method yields the spiro-hydrocarbon, 1 : 2 : 3 : 4-tetrahydrophenanthrene-2:2--spiro-*cyclo*pentane (V R=H). The latter on selenium dehydrogenation

(IV)   (V)   (VI)

gives only chrysene. It is quite likely that traces of 1 : 2-benzanthracene (VI, R=H) that might have been formed had escaped detection.

In a similar maner the spiro-hydrocarbon (V, R=Me) has also been synthesised. The anhydride of *cyclo*pentane-1-carboxy-1-acetic acid condenses with α-methylnaphthalene, forming only one keto-acid. The keto-acid on oxidation with sodium hypochlorite gives 4-methyl-1-naphthoic acid and hence it is $\alpha\alpha$-*cyclo*pentane-β-(4-methyl)-1-naphthoylpropionic acid (I, R=Me). As noted before (*J. pr. Chem.*, 1939, **152**, 11), due to the presence of a methyl group in *para*-position to the keto group, the reduction of the keto-acid (I, R=Me) to $\alpha\alpha$-*cyclo*pentane-γ-(4-methyl)-1-naphthylbutyric acid (III, R=Me) could only be accomplished when the low melting methyl ester of the keto-acid was used for reduction. On cyclisation with 85% sulphuric acid the naphthylbutyric acid (III, R=Me) gives 1-keto-9-methyl-1 : 2 : 3 : 4- tetrahydrophenanthrene-2 : 2-spiro- *cyclo*pentane (IV, R=Me). This spiro-ketone on reduction by the Clemmensen method gives 9-methyl-1:2:3:4-tetrahydrophenanthrene-2:2-spiro-*cyclo*pentane (V, R=Me). Curiously enough the ring transformation during the dehydrogenation of this spiro-hydrocarbon leads to the preferential formation of the linear anthracene

derivative, 3-methyl-1 : 2-benzanthracene (VI, R=Me) instead of the angular chrysene derivative.

EXPERIMENTAL.

αα-cyclo*Pentane-β-1-and* αα-cyclo*Pentane-β-2-naphthoylpropionic Acids* (I, R=H and II).—A mixture of the anhydride of cyclopentane-1-carboxy-1-acetic acid (31 g.) and naphthalene (40 g.) was slowly added to an ice-cooled solution of aluminium chloride (52 g.) in nitrobenzene (150 c.c.). The mixture was kept in the ice-bath for 4 hours and then at the room temperature for 12 hours. The product was decomposed with ice and hydrochloric acid and nitrobenzene and excess of naphthalene were distilled off in steam. The solid product was extracted with sodium carbonate solution, from which the mixture of keto-acids separated on acidification. This was thoroughly washed with hot water and crystallised from glacial acetic acid. The first crop recrystallised from alcohol (charcoal) in colourless needles, m.p. 190-91°, yield 2·1 g. (Found : C, 76·5 ; H, 6·4. $C_{18}H_{18}O_3$ requires C, 76·6 ; H, 6·4 per cent). The acetic acid mother-liquor was diluted with three times its own volume of hot water, boiled with animal charcoal and filtered. The keto-acid, that separated out on cooling, was repeatedly crystallised from spirit, m.p. 135-40°. This impure acid was converted into the methyl ester by methyl alcoholic hydrogen chloride. The solid methyl ester after repeated crystallisation from petroleum ether (b.p. 50-60°) gave the pure substance, m.p. 69-70°, yield 5·5 g. (Found : C, 77·0 ; H, 6·7. $C_{19}H_{20}O_3$ requires C, 77·0 ; H, 6·8 per cent). The lower melting keto-acid was obtained in a pure condition by the hydrolysis of the methyl ester and was crystallised from rectified spirit in fine needles, m.p. 140-41°. (Found : C, 76·58 ; H, 6·35. $C_{18}H_{18}O_3$ requires C, 76·6 ; H, 6·4 per cent).

The *methyl ester* of the higher melting keto-acid, prepared by methyl alcoholic hydrogen chloride, crystallised from petroleum ether (b.p. 90-100°) in prismatic needles, m.p. 109-10°. (Found : C, 76·8 ; H, 6·9. $C_{19}H_{20}O_3$ requires C, 77·0 ; H, 6·8 per cent).

Oxidation of the Keto-acid (m.p. 190-91°) *with Sodium Hypobromite Solution.*—The keto-acid (0·5 g.) was dissolved in 10% caustic soda solution and treated with sodium hypobromite solution (1·5 c.c. of bromine and 150 c.c. of 10% caustic soda solution) first in the cold and then warming on the water-bath for 1 hour. The solution was filtered and acidified with sulphurous and sulphuric acids. The separated solid was crystallised from spirit in needles, m.p. 182° (mixed m.p. with β-naphthoic acid).

The oxidation of the keto-acid (m.p. 140-41°) was carried out in a similar manner and the naphthoic acid, so obtained, after crystallisation from spirit melted at 160° (mixed m.p. with α-naphthoic acid).

αα-cyclo*Pentane*-γ-1-*naphthylbutyric Acid* (III, R=H).—αα-*cyclo*-Pentane-β-1-naphthoylpropionic acid (6 g.) was gently boiled with amalgamated zinc (30 g.) and hydrochloric acid (30 c.c.) for 24 hours. The product was extracted with ether, ether removed and the residue purified by extraction with sodium carbonate solution and precipitation with hydrochloric acid. The pasty mass, thus obtained, distilled above 200° under high vacuum as a thick liquid. The distillate on cooling and stirring with petroleum ether (b.p. 50-60°) readily solidified. It was crystallised from petroleum ether (b.p. 50-60°) in needles, m.p. 108-9°. (Found : C, 80·4 ; H, 7·5. $C_{18}H_{20}O_2$ requires C, 80·61 ; H, 7·46 per cent).

1-*Keto*-1:2:3:4-*tetrahydrophenanthrene*- 2:2-*spiro*-cyclopentane (IV, R= H).—αα- *cyclo*Pentane-γ-1-naphthylbutyric acid (3.5 g.) was cyclised with concentrated sulphuric acid (10·5 c.c.) and water (3·5 c.c.) at 100°. The product was obtained as a thick light yellow oil, b.p. 215°/6 mm., yield 2·4 g. (Found : C, 86·2 ; H, 7·3. $C_{18}H_{18}O$ requires C, 86·4; H, 7·2 per cent).

1 : 2 : 3 : 4-*Tetrahydrophenanthrene*-2:2-*spiro*-cyclopentane (V, R=H).— The foregoing spiro-ketone (2·5 g.) was heated with amalgamated zinc (15 g.) and concentrated hydrocholoric acid (15 c.c.) for 24 hours. The product was obtained as a colourless oil, b.p. 190-95°/8 mm., yield 2 g. (Found : C, 91·2 ; H, 8·6. $C_{18}H_{20}$ requires C, 91·5 ; H, 8·5 per cent).

Selenium Dehydrogenation of 1:2:3:4-*Tetrahydrophenanthrene*-2:2-*spiro*-cyclopentane.—The spiro-hydrocarbon (1·8 g.) was heated with selenium (3·5 g.) in a metal-bath at 300-20° for 12 hours and at 340-50° for 24 hours. The product was extracted with chloroform and after removal of the solvent the residue was distilled over sodium under reduced pressure, when the distillate was obtained as a white solid. This was crystallised from hot benzene in shining flakes, m.p. 249° (mixed m.p. with chrysene). (Found : C, 94·6 ; H, 5·3. Calc. for $C_{18}H_{12}$: C, 94·75 ; H, 5·25 per cent).

αα-cyclo*Pentane*-(β-4-*methyl*)-1-*naphthoylpropionic Acid* (I, R=Me).— It was prepared as in the case of αα-*cyclo*pentane-β-1-naphthoylpropionic acid, from the anhydride of *cyclo*pentane-1-carboxy-1-acetic acid (31 g.), α-methylnaphthalene (30 g.) and aluminium chloride (54 g.), in nitrobenzene (150 c.c.) solution. The product was crystallised from glacial acetic acid (charcoal) and finally from alcohol, in which it is sparingly soluble, in colourless octahedra, m.p. 176-77°. (Found : C, 77·0; H, 6·9. $C_{19}H_{20}O_3$ requires C, 77·0 ; H, 6·8 per cent),

The *methyl ester*, prepared by the action of methyl alcoholic hydrogen chloride, was crystallised from petroleum ether (b.p. 50-60°) in cubes, m.p. 56-57°, yield 24 g. (Found : C, 77·2 ; H, 7·2. $C_{20}H_{22}O_3$ requires C, 77·4 ; H, 7·1 per cent). •

Oxidation of the Keto-acid (I, R = Me) *with Sodium Hypochlorite Solution.*—The keto-acid (1·2 g.) was boiled with sodium hypochlorite solution (from 100 c c. of 10% caustic soda solution and chlorine from 2·1 g. of potassium permanganate and 15 c.c. of concentrated hydrochloric acid), and the solution was cooled, filtered and acidified with sulphurous and sulphuric acids. The product was crystallised from acetic acid in needles, m.p. 175-76°, which gave no depression with 4-methyl-1-naphthoic acid, prepared by Mayer and Sieglitz's method (*Ber.*, 1922, 55, 1839).

αα-cycloPentane-γ-(4-methyl)-1-naphthylbutyric Acid (III, R = Me).—The methyl ester of the foregoing keto-acid (I, R = Me) was gently boiled for 24 hours with amalgamated zinc (100 g.) and concentrated hydrochloric acid (100 c.c.). The product was extracted with ether, the solvent removed and the residue distilled as a thick oil (13 g.) at 230-35°/5 mm. This was hydrolysed with alcoholic potash when 11·5 g. of the reduced acid was obtained. It crystallised from petroleum ether (b.p. 70-80°), m.p. 112°. ⸍Found : C, 81·1; H, 7·7. $C_{19}H_{22}O_2$ requires C, 80·9 ; H, 7·8 per cent⸗.

9-Methyl-1-keto-1 : 2:3:4-tetrahydrophenanthrene-2:2 - spiro - cyclopentane (IV, R = Me).—The foregoing butyric acid (5 g.) was cyclised by heating on the steam-bath with concentrated sulphuric acid (15 c.c.) and water (5 c.c.) for 1½ hours. The solid product was crystallised from petroleum ether (b.p. 40-60°) in granules, m.p. 97°. (Found: C, 86·2; H, 7·7. $C_{19}H_{20}O$ requires C, 86·4 ; H, 7·6 per cent).

9-Methyl-1 : 2:3:4-tetrahydrophenanthrene-2:2-spiro-cyclopentane (V, R = Me).—The spiro-ketone (IV, R = Me) (3·5 g.), amalgamated zinc (20 g.) and concentrated hydrochloric acid (20 c.c.) were allowed to stand at the ordinary temperature overnight and then gently boiled for 24 hours. The solid product was crystallised from petroleum ether (b.p. 40-60°) in long needles, m.p. 69-70°. (Found : C, 91·1 ; H, 8·8. $C_{19}H_{22}$ requires C, 91·2 ; H, 8·8 per cent).

Selenium Dehydrogenation of 9-Methyl-1:2:3:4-tetrahydrophenanthrene-2:2-spiro-cyclopentane.—The spiro-hydrocarbon (2·3 g.) was heated with 3 g. of selenium in a metal-bath at 280-320° for 8 hours and at 340-50° for 24 hours. The product was extracted with chloroform, the solvent evaporated and the residue was distilled over sodium. The distillate was collected at 240-50°/6 mm., as a thick oil which slowly solidified. The product was crystallised from benzene-petroleum (b.p. 50-60°) mixture in

clusters of short needles, m.p. 152-53°. The mixed m.p. with a sample of 3-methyl-1:2-benzanthracene prepared according to Cook (*J. Chem. Soc.*, 1930, 1088) was 153°. (Found : C, 94·1 ; H, 5·8. Calc. for $C_{19}H_{14}$: C, 94·2; H, 5·8 per cent).

The author desires to express his grateful thanks to Dr. M. Qudrat-i-Khuda for giving facilities to carry out this work in the Presidency College Chemical Laboratory, Calcutta and to Dr. J. C. Bardhan for his kind interest in this investigation.

SYNTHETICAL INVESTIGATIONS IN THE CAMPHANE SERIES. PART V. SYNTHESIS OE ETHYL BICYCLO-(1:2:2)-HEPTANEDIONE DICARBOXYLATE FROM ETHYL *CYCLOPENTANONE*-2:5-DICARBOXYLATE.

By P. C. Guha and G. D. Hazra.

The monosodium salt of ethyl *cyclo*pentanone-2 : 5-dicarboxylate has been reacted with one molecule of ethyl bromoacetate to yield *cis*- and *trans*-ethyl 2 : 5-dicarbethoxy-*cyclo*pentanone-5-acetate, which on Dieckmannisation yields a product, containing bi*cyclo*-(1 : 2 : 2)-heptanedione-dicarboxylic ester. The latter on hydrolysis and decarboxylation yields bi*cyclo*(1 : 2 : 2)-heptanedione carboxylic acid.

Ethyl *cyclo*pentanone-2:5-dicarboxylate (I) (*Ber.*, 1936, **69**, 1212) was prepared in this laboratory in connection with earlier experiments on synthesis of *nor*thujane derivatives. The method has been further improved and the yield raised to about double the previous yield. With the improvement effected in the method of preparation, it occurred to us to try whether this substance, with two active hydrogen atoms, could be utilised as a starting material for the synthesis of bicyclic compounds of the camphane series.

The mono-sodium derivative of ethyl *cyclo*pentanone dicarboxylate (I) reacts with one molecule of ethyl bromoacetate to yield two isomeric forms (*cis* and *trans.*, II) of ethyl 2:5-dicarbethoxy-*cyclo*pentanone-5-acetate: (*i*) b.p. 145-60°/3 mm.; (*ii*) b.p. 202-30°/3 mm. The lower boiling ester passes over slowly to the higher boiling one during distillation. It has not been possible to establish definitely which of them is *trans* and which *cis*, due to the instability of the corresponding tri-acids formed during hydrolysis, both of the esters giving rise to *cyclo*pentanone-2-acetic acid (III). The *cyclo*pentanone triester (II) on treatment with sodium in benzene suspension yields a product containing bi*cyclo*-(1:2:2)-heptanedione dicarboxylic ester (IV, R and R_1 = CO_2Et) which could not be isolated from the product of Dieckmannisation, as it could not be distilled undecomposed even under 2 mm. pressure.

CH₂—CH—CO₂Et
>CO
CH₂—CH—CO₂Et

(I)

CH₂—C(H)—CO₂Et
>CO
CH₂—C—CH₂—CO₂Et
CO₂Et

(II, *cis* and *trans*)

$$
\begin{array}{l}
CH_2\text{—}CH_2 \\
\qquad\qquad >CO \\
\cdot CH_2\text{—}CH\text{—}CH_2\cdot CO_2H
\end{array}
$$

$$
\begin{array}{l}
CH_2\text{—}CH\text{—}CO \\
\qquad\quad |\quad\;\; | \\
\qquad\quad CO \\
\qquad\quad | \\
CH_2\text{—}C\text{—}CH \\
\qquad\;\; | \quad\;\; | \\
\qquad\;\; R_1 \quad R
\end{array}
$$

(III)   (IV)

The product containing (IV, R and $R_1 = CO_2Et$) on being boiled with hydrochloric acid (1:4) yields bicyclo-(1:2:2)-heptanedione carboxylic acid (IV, $R_1 = CO_2H$; R=H). It is interesting to note that Kötz (*Annalen*, 1900, **350**, 229) in his attempt to cyclise ethyl *cyclo*pentanone-2-acetate to the bicyclic.compound (IV, R and R_1=H) could only obtain the bicyclopentyl-acetone derivative (V, R = CO_2Et). It is thus clear that Dieckmannisation of (II) to give rise to the bicyclic compound (IV, R and $R_1 = CO_2Et$) has been possible due to the presence of two more additional carbethoxy groups

$$
\begin{array}{l}
CH_2\text{—}CH\text{—}CH_2 \\
\qquad\quad | \\
\qquad\quad CH_2 \\
\qquad\quad | \\
CH_2\text{—}C\text{—}CH_2 \\
\qquad\;\; | \\
\qquad\;\; CO_2H
\end{array}
\;\rightarrow\;
\begin{array}{l}
CH_2\text{—}CH_2 \\
\qquad\quad | \\
\qquad\quad CO \\
\qquad\quad | \\
CH_2\text{—}CH\text{—}CH_2\cdot CO.CH\text{—}
\end{array}
\begin{array}{l}
CH_2\text{—}CH_2 \\
\qquad\quad | \\
\qquad\quad CO \\
\qquad\quad | \\
CH\text{—}CH_2 \\
| \\
R
\end{array}
$$

(VI)   (V)

in (II). The isolation of the bicyclic diketo-acid (IV, $R_1 = CO_2H$; R = H) from (IV, R and $R_1 = CO_2Et$) on hydrolysis, lends further support to the view that the cyclisation has not proceeded in the direction as observed by Kötz in which case the compound corresponding to (V, R=CO_2Et) would have yielded a triketo compound (V, R=H) by complete decarboxylation. The equivalent of the acid (IV, R=H; $R_1 = CO_2H$) has been determined and its ethyl and methyl esters as also the semicarbazone of the methyl ester prepared. With a view to obtaining the reduced *nor*bornylene carboxylic acid (VI), the bicyclic diketo-acid (IV, R=H; $R_1 = CO_2H$) has been reduced according to the method of Clemmensen to an acid melting at 118° which could not be combusted nor further examined due to the yield being extremely poor.

Work is in progress to convert (IV, R=H; $R_1 = CO_2H$) into *nor*bornylene *via* (VI) and experiments on ring-closure of alkyl derivatives of ethyl methyl*cyclo*-pentanone-dicarboxylate are also contemplated. ...

EXPERIMENTAL.

Improved Method of Preparation of Ethyl cycloPentanone-2:5-dicarboxylate (I).—A mixture of ethyl butane tetracarboxylate (129 g.), molecular sodium (9·6 g.) and dry benzene (500 c.c.) was boiled under reflux for

2 hours. After cooling to 0°, the reaction mixture was acidified with sulphuric acid. The benzene layer after being washed with water was dried and freed from benzene by distillation, the residue distilled under reduced pressure and the fraction b. p. at 139-40°/2 mm. collected, yield 58 g. To ensure proper yield, it is necessary to distil small quantities at a time. The yield of this compound according to the method of Nandi (*J. Indian Chem. Soc.*, 1934, 11, 279), by the use of sodium ethoxide as the cyclising agent, was 30 g. from 130 g. of ethyl butantetracarboxylate.

Action of Ethyl Bromoacetate on Compound (I): *Isolation of Ethyl* cyclo*Pentanone-2:5-carbethoxy-5-acetate* (II).—The cyclopentanone ester (I, 68·4 g.) was added to molecular sodium (6·9 g.), suspended in dry benzene, when the sodium derivative was mostly formed; towards the end, it was warmed for about 1 hour for completion of the reaction To the sodium derivative, ethyl bromoacetate (100 g.) was added gradually under shaking. It was allowed to stand for 72 hours at room temperature, then heated on a water-bath for 2 hours when the reaction product became neutral. After cooling it was acidified with 10% sulphuric acid and the benzene layer was freed from the solvent by distillation on a water-bath and the residue subjected to steam distillation. The residue was distilled under reduced pressure and the following fractions separately collected : (*i*) b.p. up to 135°/3 mm., yield 15 g.; (*ii*) b.p. 135-42°/3 mm., yield 8 g.; (*iii*) b.p. 145-202°/3 mm., yield 9 g.; (*iv*) b. p. 202-30°/3 mm., yield 40 g. The residue did not boil at a constant temperature and hence was rejected. The last fraction (*iv*) on redistillation gave a portion boiling at 202-8°/3 mm., yield 35 g. (Found : C, 57·41 ; H, 8·19. $C_{15}H_{20}O_7$ requires C, 57·32 ; H, 7·0 per cent). It gives a purple colouration with ferric chloride.

The fraction (*iii*) on repeated distillation gave an oil, b.p. 202-208°/3 mm. and containing C, 56·69 ; H, 7·97 per cent. When the preparation of the compound (II) was tried in alcoholic medium, the reaction product was obtained as a gum and could not be purified by distillation. It was also noticed that the use of one molecule of ethyl bromoacetate was not conducive to good yield, some of the cyclopentanone ester (I) remaining unreacted.

The fraction (*iii*) (4 g.) was heated with 18% hydrochloric acid (40 c.c.) under reflux for 4 hours. After steam distillation, the clear solution was evaporated to dryness on a water-bath when an oily substance was left behind which on being kept at 0° in a vacuum desiccator gave a semi-solid, which completely solidified on being kept on a porous plate in a vacuum desiccator. This crystallised from a mixture of ether and alcohol, m.p. 50°. The ethyl ester was prepared in the usual manner, b.p. 130°/18 mm. The semicarbazone of the ester melted at 174° and was proved to be identical

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with the semicarbazone of ethyl *cyclo*pentanone-2-acetate, by taking mixed m.p. with a genuine sample. The fraction (*iv*) on similar treatment gave an acid melting at 50°; ethyl ester, b.p. 130°/18 mm., giving a semicarbazone, m.p. 174° (Kötz, *Annalen*, 1904, **350**, 229).

Cyclisation of Compound (II): *Formation of Ethyl Bicyclo-(1:2:2)-heptane-dione-dicarboxylate* (IV, R and $R_1 = CO_2Et$).—A mixture of ester (II, 30 g.; b.p. 202-8°/3 mm.), molecular sodium (2·5 g.) and benzene (200 c.c.) was heated under reflux during 3 hours. After cooling the reaction mixture was acidified with 10% sulphuric acid. The benzene layer after drying was found to decompose on attempting distillation under reduced pressure; hence the product was used as such for the next operation.

Hydrolysis and Decarboxylation of the above Ester: Formation of Bicyclo-(1:2:2)-heptane-dione-carboxylic Acid (IV, R = H ; $R_1 = CO_2H$).—The ester obtained in the foregoing operation was directly hydrolysed with 8% hydrochloric acid by heating under reflux for 12 hours. After extraction of the reaction product with benzene, the acidic solution on evaporation gave rise to (*i*) a crystalline substance (2 g.), and (*ii*) a viscous mass. The crystalline product was recrystallised thrice from water, m.p. 212°. (Found: C, 51·8; H, 6·2; Equiv., 189. $C_8H_8O_4$, H_2O requires C, 51·6; H, 5·4 per cent. Equiv., 186). 0·104 G. of substance lost 0·0074 g. of water at 200° ; hence the substance contains one molecule of water of crystallisation. The viscous mass gave an acidic semicarbazone, m p. 192°. (Found: N, 20·7. $C_8H_{13}O_3N_3$ requires N, 21·1 per cent).

Methyl Ester of the Bridged Diketo-acid (IV, R = H ; $R_1 = CO_2H$).—The acid (1 g) was dissolved in dry ether and a dry ethereal solution of diazomethane was added to it. The ether and the excess of diozomethane was removed under suction. The residual solid crystallised from methyl alcohol, m.p. 129°, yield 0·6 g. Half of it was hydrolysed with hydrochloric acid (1:1), when an acid, m.p. 212°, was obtained, and was proved to be identical with the original acid by mixed m.p. The remaining half of the methyl ester was converted into the semicarbazone which crystallised from methyl alcohol, m.p. 209-10° (Found: N, 27·92. $C_{11}H_{16}O_4N_6$ requires N, 28·3 per cent).

Clemmensen Reduction of Acid (IV, R = H ; $R_1 = CO_2H$).—The acid (1 g.) was reduced according to Clemmensen's method with zinc wool and hydrochloric acid and on being worked up as usual, gave a small quantity of an acid, m.p. 118°. As the amount of this compound was very small its combustion could not be performed.

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ON THE OSMOTIC RELATIONSHIPS. BETWEEN EGG-WHITE AND EGG-YOLK AND THE EFFECTS OF INJECTION OF POTASSIUM CYANIDE AND SODIUM FLUORIDE THEREON.

BY N. M. BASU AND M. C. MITRA.

The average difference in freezing point between egg-yolk and egg-white has been found to be 0·07°. Sodium fluoride solution has been injected underneath the shell and the effects of this injection on the difference in freezing point are noted for 72 hours, showing that the difference in freezing point is reduced from day to day. This difference is accordingly concluded to be not due to Donnan equilibrium between the two sides of the vitellin membrane but is due to a "dynamic steady state" maintained by the vitality of the membrane. The results of injection of potassium cyanide are anomalous and an explanation has been suggested.

A considerable difference in the freezing point between egg-yolk and egg-white was noticed by Straub (*Rec. trav. chim.*, 1929, **48**, 49) and this difference is maintained, if the white be diluted and then left in contact with the yolk for 48 hours and exists even if the diluted egg-white be replaced by undiluted egg-white and left in contact with the same yolk for another 48 hours. Hill (*Trans. Faraday Soc.*, 1930, **26**, 667) showed that the difference in osmotic pressure between yolk and white is roughly about two atmospheres and that the membrane separating the yolk from the white, known as the " vitellin membrane " is extremely thin and permeable to water and the salts of yolk; yet the yolk and the white are not in osmotic equilibrium. The osmotic difference between yolk and white gradually diminishes with age, but the difference is maintained whether the eggs are kept in air or free from oxygen. According to Hill (*loc. cit.*) no true equilibrium exists between the inside and outside of the yolk but a dynamic steady state is maintained as in the case of the nerve or the muscle-fibre. In the case of a nerve or muscle-fibre the potential difference between the inside and the outside is much greater than what can be due to Donnan membrane equilibrium and is maintained so long as oxidation is possible. Accordingly it is concluded that in a nerve or muscle-fibre there is no true equilibrium between the inside and the outside of the fibre, but a dynamic steady state is maintained by oxidation. Johlin (*J. Gen. Physiol.*, 1932, **16**, 605) found considerable difference in osmotic pressure between the yolk and the white of newly laid eggs but he considered unnecessary the postulation

of a vital activity maintaining a steady state on account of slow establishment of the osmotic equilibrium.

In the present paper attempt has been made to re-examine the whole problem and to find out the effects of injection of potassium cyanide and sodium fluoride on the dynamic steady state, if any, between the yolk and the white, as these reagents are well known inhibitors of oxidation, potassium cyanide inhibiting most types and sodium fluoride inhibiting all types of oxidation.

If the difference in freezing point between the yolk and the white be entirely due to Donnan membrane equilibrium, the disappearance of the biological activity, if any, of the vitellin membrane will not affect it. Accordingly the injection of sodium fluoride, which inhibits the activity of all forms of life, maintained by oxidation, will not affect this difference in freezing point except in so far as would be caused by the distribution of the injected sodium fluoride between the yolk and the white.

If the difference in freezing point be due to dynamic steady state maintained by the biological activity of the vitellin membrane, then, after the injection of sodiun fluoride, the difference in freezing point is expected to be reduced.

EXPERIMENTAL.

A number of fresh eggs was taken. In some of them the freezing points of yolk and white were determined so that the average difference in freezing point between the yolk and the white was found. The remaining eggs were divided into two groups, one group being left for control and the eggs in the other group were injected with o·5 c.c. of a solution containing o·1 g. of sodium fluoride. Before the injection a hole was made with a sterilised needle on the shell, then o·5 c.c. of egg-white was removed with a sterilised syringe and the same amount of sodium fluoride solution injected underneath the shell. The hole was immediately plugged with aseptic cotton and collodion. All the eggs were then left in the frigidaire. After 24 hours a control egg and an injected egg were taken out and the freezing points of yolk and white of each were determined. The same process was repeated after 48 hours and 72 hours.

Some difficulty was experienced in the determination of the freezing point of egg-yolk (cf. Johlin, loc. cit.). When the temperature of the yolk approaches the freezing point, it becomes so viscous that the platinum stirrer, provided with the instrument, detaches itself from the glass rod

TABLE I.

Egg No.	Date of Purchase.	Date of Exam.	Volume of White. 20 c.c.	Volume of Yolk. 15 c.c.	Diff. 5 c.c.	Freezing point of Yolk.	Freezing point of White.	Diff.	Remarks
I	8-4-37	8-4-37	20	15	5	0·47	0·4	0·07	After purchase eggs were kept in frigidaire so as to prevent decomposition.
II	,,	10-4-37	20	15	5	0·56	0·53	0·03	After 4 days the same difference in F.P. was maintained.
III	,,	12-4-37	16	11·5	4·5	0·48	0·41	0·07	
IV	30-4-37	30-4-37	16	9	7	0·65	0·58	0·07	After 24 hours the same difference in F.P. was maintained.
V	20-4-37	21-4-37	15	10	5	0·48	0·41	0·07	
VI	,,	,,	15·5	10·5	5	0·53	0·51	0·02	Injected with 0·5 c.c. of NaF solution containing 0·1 g. of NaF (0·5% soln. of NaF acts as an inhibitor to oxidising enzymes). The diff. in F.P. was reduced after 24 hours.
*VII	,,	22-4-37	15	10	5	0·57	0·5	0·07	After 48 hours the same difference in F.P. existed
VIII	,,	,,	16·5	10·5	6	0·55	0·53	0·02	Injected with NaF soln. on 20-4-37. The diff. in F.P. was reduced after 48 hours.
IX	,,	,,	20	15	5	0·47	0·455	0·015	Injected with NaF soln on 20-4-37. The diff in F.P. was reduced after 48 hours.
X	,,	23-4-57	20	15	5	0·47	0·4	0·07	After 72 hours the difference in F.P. still existed.
XI	,,	23-4-37	17·5	12	5·5	0·54	0·53	0·01	Injected with NaF soln on 20-4-37. The difference in F.P. was further reduced after 72 hours.
XII	12-4-37	16-4-37	20	15	5	0·59	0·52	0·07	After 4 days the same difference in F.P. existed.
XIII	,,	,,	20	15	5	0·62	0·51	0·11	Injected with 0·5 c.c. of KCN soln. containing 1 mg. KCN. After 4 days the diff. in F.P. increased

* An opening was made in egg No VII aseptically and immediately closed by collodion and cotton and then kept in frigidaire.

TABLE I (*contd.*).

Egg No.	Date of Purchase.	Date of Exam.	Volume of White.	Volume of Yolk.	Volume Diff.	Freezing point of Yolk.	Freezing point of White.	Diff.	Remarks.
XIV	12-4-37	16-4-37	20 c.c.	15 c.c.	5 c.c.	0·61	0·51	0·1	After 4 days the diff. in F.P. increased.
Duck's eggs.									
A	7-9-37	8-9-37	32	24	8	2·035	1·995	0·04	Examined after 24 hours.
B	,,	,,	36	25	11	2·24	2·1715	0·0685	,, ,, Injected with 1 c.c. of KCN soln. containing 4 mg. of KCN.
C	,,	9-9-37	32	24	8	2·055	2·015	0·04	Examined after 48 hours. The same difference existed.
D	,,	,,	37	25	12	2·075	2·007	0·068	,, ,, Injected with KCN soln.
E	,,	10-9-37	35	23	12	2·035	1·99	0·045	Examined after 72 hours. Almost the same difference existed.
F	,,	,,	—	—	—	2·0475	1·98	0·0675	Examined after 72 hours. Injected with KCN soln. Two readings viz. 2·05 and 2·045 were obtained for yolk, the mean, viz. 2·0475 was taken.

G To the white of egg No. E, 1 c.c. of KCN solution containing .4 mg. of KCN was added and the change in F.P. after the addition was noted. It was found that the F. P. increased from 1·99 to 2.

N.B. It is curious that after the injection of KCN to eggs of duck or chicken the difference in F.P. between the yolk and the white increased instead of being diminished. *Vide* eggs no. XIII, B, D and F.

In the experiments noted above care was taken to keep the total amount of the mercury in the bulb constant, when the freezing points of yolk and white of the same egg were determined. The actual zero point was not determined, as the difference in freezing point between yolk and white was noted in these experiments.

during brisk stirring. In order to effect brisk stirring for ensuring uniform freezing throughout the whole liquid, a glass spiral stirrer was made, the length of the spiral being a little less than the column of liquid taken in the inner tube. The yolk was also churned into a homogeneous mass before its freezing point was determined. This is essential for getting consistent results.

Experiments were also made in the same way after the injection of potassium cyanide solution. In the eggs of chicken 0·5 c.c. of solution containing 1 mg. of potassium cyanide was injected. As the results obtained were unexpected, the same experiment was repeated with duck's eggs. In these 1 c.c. of solution containing 4 mg. of potassium cyanide was injected. Before the injection an equal amount of egg white was sucked out by a sterilised syringe.

The results of experiments are given in Table I.

DISCUSSION.

It is obvious from experiments with eggs No. I, III, IV, V, VII, X, and XII that the average difference in F..P. between the yolk and the white, *viz.*, 0·07°, is maintained after 24 hours, 48 hours and also after 96 hours, even if the egg be punctured aseptically and then immediately plugged by cotton and collodion and kept in a refrigerator (*vide* egg No. VII in the Table). Johlin's statement that the osmotic equilibrium is slowly established is not borne out by facts, at least in the case of eggs which were kept in the frigidaire for inhibiting slow decomposition which takes place in air at the ordinary temperature of the laboratory. In egg No. II the difference in the freezing point is only 0·03°. This small difference in freezing point is also noticed in the case of eggs which are not quite fresh. This egg was probably not fresh when it was purchased

After the injection of sodium fluoride the freezing point of egg-white would be greater than before and, therefore, the difference in freezing point between yolk and white would be less. But as sodium fluoride diffuses into the yolk the concentration of sodium fluoride diminishes in white and increases in yolk. Accordingly the difference (in freezing point) between the yolk and the white would be gradually greater than after the injection. In course of time, while the distribution of sodium fluoride between the yolk and the white comes to an equilibrium, the difference in freezing point between the yolk and the white cannot be so small as it was immediately after the injection of sodium fluoride into the white. When 20 c.c

of the white are mixed with o·5 c.c. of sodium fluoride solution contain-
ing o·1 g. of the substance, its freezing is actually found to be
lowered by o·045° (approx.), so that after the injection of the sodium
fluoride solution the difference in freezing point between the yolk and white,
taking o·07° as the normal average difference, would be o·07-o·045 *i.e.*,
o·025°. In the experiments given above it is observed that the difference
in freezing point diminishes after 24 hours to o·02°, after 48 hours to
o·02° or o·015°, and after 72 hours to o·01° (*vide* experiments with
eggs no. VI, VIII, IX and XI). This gradual diminution in the difference
in freezing point between the yolk and the white after the injection of
sodium fluoride solution shows clearly that this difference is due to a dynamic
steady state maintained by the biological activity of the vitellin membrane,
for as soon as this is inhibited by the injected sodium fluoride
the difference begins to diminish. This marked diminution in the difference
in freezing point cannot in any way be explained as due to the injected
sodium fluoride as discussed above.

Experiments with potassium cyanide show curious results. Instead
of an expected diminution in difference in freezing point between yolk and
white, the difference increased. It is probably due to the action of
potassium cyanide after diffusion into the yolk on some of the constituents,
in consequence of which it is split up into small molecules. Accordingly
its freezing point has been much lowered and the difference between the
freezing point of yolk and white has increased.

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BIOCHEMISTRY OF *AEROBACTER AEROGENES* AND *BACILLUS CEREUS*.

By H. Chaudhuri, N. N. Chopra, Mansa Ram and J. N. Ray.

Dulcitol-negative *Aerobacter aerogenes* and dulcitol-positive *A. aerogenes* (Syn *A. Oxytocum*) have been isolated from potatoes suffering from the black centre disease, and *B cereus* from rotting 'Chiku' fruit (*Achras sapota*, L). The products of metabolism of these three organisms on carbohydrate substrates have been examined. Acetyl methyl carbinol, ethyl alcohol, acids and gases are the principal products. The influence of the nature of substrate, hydrogen ion concentration of media, the temperature of fermentation and the effect of aeration have been studied in detail.

Although micro-organisms produce plant diseases of diverse types, the biochemistry of the organisms present on diseased plants has not been extensively studied. The present paper is a report of the investigation carried out in connection with two kinds of plant diseases. The first is a pathological condition typical with potatoes and is marked by the appearance of a dark spot or ring in the centre. The second disease is met with in the fruit 'chiku' (*Achras sapota*, L.) and results in extensive breakdown of the internal cell structure of the fruit. From diseased potatoes thirteen morphologically individual organisms were isolated which produced acetylmethyl carbinol and ethyl alcohol in varying amounts. Out of these two proved to be vigorous fermenters of starch and glucose with the formation of these products. These two have been subsequently identified as a new physiological strain of *Aerobacter aerogenes*. The two differ amongst themselves in that one of them is dulcitol-positive and the other is dulcitol-negative. From the 'chiku' fruit a bacillus identified as *B. cereus* has been isolated. Both *A. aerogenes* and *B. cereus* occur widely in soils and thereby find their way into the plant and probably participate with other organisms in causing the disease.*

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* The authors are not yet in a position to state with certainty whether these two micro-organisms are the specific producers of the respective diseases in potatoes and 'chiku' fruit. They are, however, the predominant types present in the diseased tissue. Experiments are now in progress in which healthy potatoes and 'chiku' fruit will be inoculated with vigorous cultures of the *A. aerogenes* and *B. cereus* strains, in order to test if the characteristic symptoms of the two diseases can thereby be reproduced.

On a reference to literature a few observations on the metabolic products of *A aerogenes* were found (*cf.* Harden and Walpole, *Proc. Roy. Soc.*, 1906, **B**, 77, 399 ; Walpole, *ibid.*, 1911, **B**, 83, 272 ; Neuberg, Nord and Wolff, *Biochem. Z.*, 1920, 112, 144 ; Fred and Peterson, *J. Infect. Dis.*, 1920, 27, 539 ; Nagai, *Biochem. Z.*, 1923, 141, 261 ; Levy-Bruhl, Cado and Huri, *Ann. Inst. Pasteur*, 1931, 58, 498) but none in case of *B. cereus*. Even with *A. aerogenes* no systematic study has been described. Furthermore, the two strains of *A. aerogenes*, isolated by the authors from potatoes, differ from the usual types in that they do not cause a rapid evolution of gas and acid from lactose and hence they are physiologically different from the known strain. A detailed study of their metabolic products under different conditions of substrate and nutrition, temperature, hydrogen ion concentration, aeration, etc. would be interesting apart from the question of plant disease.

The isolation of the organisms was carried out as usual by scraping the diseased portion, shaking the scrapings in sterile water and plating and replating. The dilution method of isolation was resorted to and thirteen morphologically different organisms were isolated from the diseased potatoes. These individuals were regrown in nutrient agar slants adjusted to p_H 7·0 at 40°, when a vigorous growth was obtained. The pure cultures were maintained on nutrient agar slopes adjusted to p_H 7·0. Northrop, Ashe and Senior (*J. Biol. Chem.*, 1919, 39, 1) have isolated an acetone and ethyl alcohol-producing organism from old potatoes. In the earlier experiments, therefore, these two compounds were specially looked for in the metabolic products. Actually ethyl alcohol was found to be produced by all the three organisms but no acetone except in traces. On the other hand acetylmethyl carbinol was formed in practically all cases.

EXPERIMENTAL.

The preliminary experiments were carried out on a starch-peptone-calcium carbonate medium. Subsequently, however, glucose was used as the carbohydrate substrate along with various other nutrients as described under ' substrates and nutrition'. The media were contained in bottles or flasks which were sealed suitably after inoculation and incubated at the appropriate temperature for fifteen days, after which the contents were analysed.

Methods of Analysis.—For qualitative testing for the different alcohols, aldehydes, ketones, acids, etc. the usual reactions were employed. In

the quantitative analysis complication arose on account of the fact that both acetylmethyl carbinol and acetone give similar reactions with different reagents used in the analysis which depend upon the reactivity of the CH_3 CO — group, present in both the cases. However, as found by Langlyke and Peterson (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 163) acetylmethyl carbinol distils over from an aqueous solution at a constant rate independent of its concentration. Thus the amounts that distilled over in the first 50 c.c. fraction and the second 25 c.c. fraction, when 100 c.c. were distilled, were 59·7% and 23·9% respectively of the original amount present in the liquid distilled. Acetone and ethyl alcohol on the other hand distilled over rapidly and quantitatively in the first 50 c.c. of the distillate. Acetylmethyl carbinol can thus be estimated by the iodoform method in the second 25 c.c. portion of the distillate and this amount multiplied by the factor 4·18, therefore, gives the total amount present in the original liquid. The portion of the first 50 c.c. of the distillate which was expected to contain all the ethyl alcohol and acetone and 59·7% of the total acetylmethyl carbinol was also analysed by the iodoform method and after making a slight correction for alcohol it was found that the amount of acetone present in most cases was negligible. Another portion of this first fraction of the distillate was oxidised with a known excess of potassium dichromate and from the amount of dichromate consumed the amount of ethyl alcohol present was calculated after allowing for the acetylmethyl carbinol.

The dulcitol-negative and the dulcitol-positive strains of *A. aerogenes* will be referred to as *A. aerogenes* I and *A. aerogenes* II respectively.

Effect of Substrate and Nutrition.—The following three media have been studied.

A. Glucose (5%), peptone (0·5%) and calcium carbonate (2%), p 7·0.

B. Glucose (5%), ammonium phosphate (0·5%), potassium dihydrogen phosphate (0·5%), potassium phosphate (0·01%) and magnesium sulphate (0·5%), p_H 7·0.

C. Glucose (5%), peptone (0·5%), meat extract (0·3%), sodium chloride (0·5%) and calcium carbonate (2%), p_H 7·0.

50 C.c. of the media after inoculation were incubated at 26° for 15 days after which the contents were analysed.

TABLE I.

| Medium | Expt. No. | % on weight of sugar fermented | | Expt. No. | % on weight of sugar fermented | | Expt. No. | % on weight of sugar fermented | |
		Acetyl-methyl carbinol.	EtOH.		Acetyl-methyl carbinol.	EtOH.		Acetyl-methyl carbinol.	EtOH.
		A. aerogenes I			*A. aerogenes* II			*B. cereus*	
A	1	2·15	14·58	1	2·16	16·66	1	4·29	0·89
	2	1·97	14·27	2	2·23	16·81	2	4·03	1·38
B	1	2·00	3·25	1	5·45	3·21	1	3·21	1·33
C	1	2 06	11·14	1	1·58	9·17	1	4·40	3·15

It is obvious that for the production of ethyl alcohol glucose-peptone-calcium carbonate medium is more suitable than the one containing glucose and inorganic salts, although quite heavy growths were obtained even with the latter. *A. aerogenes* II gave better yield of acetylmethyl carbinol in the glucose-inorganic salt medium than the glucose-peptone-calcium carbonate one.

Effect of Hydrogen Ion Concentration.—Acids were formed during fermentation in varying amounts by all the three organisms. *A. aerogenes* strains gave more acids than *B. cereus*. The study of the influence of p_H was carried out with two media.

(A)   Glucose (5%), peptone (0·5%), calcium carbonate (2%).

(B)   Glucose (5%), ammonium phosphate (0·5%), potassium dihydrogen phosphate (0·5%), magnesium sulphate (0·5%) and potassium phosphate (0·01%).

The incubation was carried out as usual in sealed bottles at 26°.

TABLE II.

50 C.c. medium in 500 c.c. sealed flask.

Organism.	Media.	p_H.	Expt. No.	% on wt. of sugar fermented.		% of sugar fermented.
				Acetylmethyl carbinol.	Ethyl alcohol.	
A. aerogenes I	A	7 0	1	2·12	14·47	60·0
			2	1·69	15·04	60·6
		7·4	1	1·97	14·27	61·5
			2	2·15	14·58	61·0
		8·5	1	2·44	12·92	67·9
			2	2·46	11·54	69·5
A. aerogenes II	A	7·0	1	2·26	15·04	79·1
			2	2·60	15·85	80·5
		7·4	1	2·10	16·66	68·0
			2	2·23	16·81	73·2
		8·5	1	1·81	16·27	75·6
			2	2·43	17·03	77·0
B. cereus	A	7·0	1	3·33	1·32	67·8
		7·4	1	4·29	0·89	63·4
			2	4·03	1·38	65·4
		8·5	1	2·53	0·76	73·0
A. aerogenes I	B	6·2	1	8·20	3·88	100·0
		7·0	1	1·70	3·19	100·0
			2	2·30	3·33	100·0
		7·6	1	1·50	3·17	100·0
			2	1·11	2·97	100·0
A. aerogenes II	B	6·2	1	8·43	3·51	100·0
		7·9	1	5·41	3·20	100·0
		7·6	1	5·29	3·00	100·0
B. cereus	B	6·2	1	4·85	3·11	12·4
		7·0	1	3·21	1·33	49·0
		7·6	1	2·91	1·72	52·8

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Although it is difficult on account of the variable nature of the fermentations to draw accurate conclusions, yet it may broadly be stated that the optimum p_H for the production of acetylmethyl carbinol varies with the nature of the substrate. In case of glucose-peptone medium the optimum was on the whole on the alkaline side, i.e., p_H 7·5-8·5, whilst in the medium with inorganic nitrogen source, it was on the acidic side. i.e., at p_H 6·2. The same general conclusions were drawn when 50 c.c. of the medium were fermented in 250 c.c. or 500 c.c. sealed flasks, i.e., with larger volume of air.

Effect of Temperature.—The medium contained glucose, peptone and calcium carbonate. 50 C.c. of the medium were fermented in 250 c.c. sealed flasks.

TABLE III.

Organism.	Temp.	Expt. No.	% on wt. of sugar fermented.		% of sugar fermented.
			Acetylmethyl carbinol.	Ethyl alcohol.	
A. aerogenes I	26°	1	1·97	14·27	61·5
		2	2·15	14·58	61·5
	33	1	1·95	9·95	100·0
		2	1·70	12·96	100·0
	40	1	6·11	10·36	100·0
A. aerogenes II	26	1	2·10	16·66	68·1
		2	2·23	16·81	68·1
	33	1	2·58	11·13	100·0
		2	3.01	10·47	100·0
	40	1	3·69	9·81	100·0
		2	4·11	9.63	100·0
B. cereus	26	1	4·29	0·89	31·8
		2	4·13	1·38	32·7
	33	1	2·99	3·55	68·1
	40	1	6·96	3·26	83·4

The requirements of temperature for acetylmethyl carbinol production and ethyl alcohol production are inversely related to each other for A. aerogenes. Acetylmethyl carbinol is formed in largest amount at 40°, at which temperature alcohol production is minimum. The inverse is the case at 26°. For B. cereus the optimum temperature for acetylmethyl carbinol

formation is again 40° but for alcohol production it is 33°. These results have been confirmed in a second series of experiments in which the fermentation was carried out in contact with larger volume of air, *i.e.*, 50 c.c. fermented in 500 c.c. flasks.

TABLE IV.

Effect of aeration.

The media used consisted of glucose (5%), peptone (0·5%), calcium carbonate (2%), p_H 7·0.

Organism.	Expt. No.	Temp. of incuba- tion.	% of sugar fermented			
			50 C.c media in 250 c.c. flasks.		50 C.c. media in 500 c.c. flasks.	
			Acetyl- methyl carbinol.	Ethyl alcohol.	Acetyl- methyl carbinol.	Ethyl alcohol.
A. aerogenes I	1	26°	1·97	14·27	3·47	13·82
	2		2·19	14·58	—	—
A. aerogenes II	1	26	2·10	16·66	3·01	—
	2		2·23	16·81	3·37	13·12
B. cereus	1	26	4·29	0·89	13·41	2·78
	2		4·03	1·38	—	—
A. aerogenes I	1	33	1·95	11·45	2·94	—
	2		1·70	—	2.28	11·34
A. aerogenes II	1	33	2·58	11·13	2·69	11·44
	2		3·01	10·47	—	—
B. cereus	1	33	2·87	3·66	4·82	4·20
	2		3·09	4·10	—	—

Production of acetylmethyl carbinol is, therefore, favoured by increased aeration with all the three organisms at the two temperatures studied. This supports the findings of Walpole (*Proc. Roy. Soc.*, 1911, **B, 83**, 272) and Kluyver, Donker and Hooft (*Proc. Acad. Sci. Amsterdam*, 1925, **28**, 317), who have found that with *B. lactis aerogenes* and *Saccharomyces cerevisiae* respectively the yield of acetylmethyl carbinol is increased by aeration and by the addition of hydrogen acceptors such as

methylene blue. No regular effect of aeration on ethyl alcohol production can be noticed from the above data.

Further detailed work is being carried out on the biochemistry and metabolic products of *B. cereus* and will be reported in due course.

MAGNETISM AND CATALYSIS. PART I. CATALYTIC DECOMPOSITION OF POTASSIUM CHLORATE BY MANGANESE DIOXIDE AND FERRIC OXIDE.

By S. S. Bhatnagar, Brahm Prakash and Jarnail Singh.

The reaction mechanism of the catalysed decomposition of potassium chlorate with oxides are examined from the magnetic standpoint by a chemical and magetic analysis of the products at different stages of the reaction by measurements of χ The mechanism has been proved to involve the formation of an intermediate compound as shown by differences at the intervening stages of the reaction between the observed values of χ and the values calculated on the mixture law. The nature of the possible intermediate compound is discussed and the earlier theories are controverted. A modified form of Sodeau's theory of alternate oxidation and deoxidation is suggested. In the case of catalysis by ferric oxide, strict concordance is evinced between the observed and the calculated values of χ at all stages of the reaction.

It was observed by Hedvall, Hedin and Persson (*Z. physikal. Chem.*, 1934, **B27**, 196) that the thermal decomposition of nitrous oxide, using nickel as a catalyst, was suddenly accelerated above the Curie point, although *X*-ray analysis by Nunzio (*Atti. R. Inst. Veneto*, 1933, 92, 541) does not indicate any change in lattice-structure above this temperature. An extension of the work by Hedvall and others (*Z. physikal. Chem.*, 1937, **B30**, 280) has shown that the hydrogenation of carbon monoxide and acetylene in the presence of nickel, and the formation of CO_2 from CO by Heusler's alloy is considerably accelerated at the Curie point. Forestier and Lille (*Compt. rend.*, 1937, **204**, 265, 1254) who studied the catalytic power of ferrites of Mg, Cu, Sr, Ba and Pb, found anomalies at the Curie point accompanied by a marked rise in catalytic power in the neighbourhood of this temperature. The fact that catalytic activity may have some relation to magnetic properties was also emphasised by Taylor and Diamond (*J. Amer. Chem. Soc.*, 1935, **57**, 1251), who found that the spin isomerisation of hydrogen at low temperatures is much more catalysed by a paramagnetic surface than by a diamagnetic one. Apart from this little use has been made of the magnetic method in deciding the mechanism of the catalytic changes, particularly those where the formation of an intermediate compound is postulated.

A case in point is the catalysed decomposition of potassium chlorate with oxides. It has been suggested from time to time that the action is

purely mechanical but if it were so, all other finely divided substances, irrespective of their chemical composition, should be expected to act in a similar manner which, however, is not the case. Besides, a microscopic examination of MnO_2, before and after the reaction, shows that the dioxide has undergone a physical change which leads to the conclusion that the forces involved in the reaction are chemical in nature. If the decomposition takes place *via* an intermediate compound, then its formation (if it is stable) in the intermediate stages, even though it may not be revealed by chemical analysis, would be shown by magnetic analysis of the reaction products particularly if the development of the new compound entails changes in valency. That changes in valency produce corresponding changes in magnetic moment which can be correlated with atomic structure, has been emphasised by several workers, notably Van Vleck ("Theory of Electric and Magnetic Susceptibilities," Oxford, particularly Chapter XI, p. 73), Sommerfeld ("Atombau," 4th Edition, p. 639), Bose (*Z. Physik.*, 1927, **43**, 864) and Stoner (*Phil. Mag.*, 1929, **8**, 250) who have obtained the following relationship in the case of the paramagnetic ions of transition elements :

$$\mu_B = \sqrt{4S(S+1)},$$

the value of μ_B depending on S and ultimately on the valency of the ion.

The main object of the present investigation is to ascertain the reaction mechanism by a magnetic and chemical analysis of the products at various stages of the reaction and to test the validity of the numerous theories of this action which have been advanced from time to time.

EXPERIMENTAL.

The susceptibility values were determined on a modified form of Gouy's magnetic balance and the calculation of χ made according to the equation,

$$\chi_{p_2} = \frac{1}{m_{p_1}} \left\{ (\chi_{p_1} \ m_{p_1} - \chi_a \ m_{ap_1}) \frac{W_{p_2}}{W_{p_1}} + \chi_a \ m_{ap_2} \right\}$$

where χ_{p_1} and χ_{p_2} are respectively the specific susceptibilities of the standard substance and of the specimen, W_{p_1} and W_{p_2} are the respective pulls, m_{p_1} and m_{p_2} are the respective masses and m_{ap_1} and m_{ap_2} are the masses of air displaced respectively by the standard substance and by the specimen.

Materials Used.

Potassium Chlorate.—The extra pure salt was recrystallised and its purity ascertained by reducing it to the chloride with sulphur dioxide and estimating the chloride by Volhard's method (% purity = 99·80). The chlorate gave a susceptibility value of $-0·300 \times 10^{-6}$ (cf. $\chi = -0·300$, International Critical Tables).

Manganese Dioxide.—Many attempts have been made to obtain pure manganese dioxide and it has been shown that it cannot be obtained pure by any of the precipitation methods since the hydrated dioxide very readily loses part of its oxygen and thus forms mixtures of oxides. Various other methods for the preparation of MnO_2 were examined and ultimately the catalyst was prepared by heating manganous nitrate at $155-60°$ for 50 hours. The black crystalline oxide was washed and dried under vacuum at $200°$. Its oxidising power was determined by treating the oxide with hydrochloric acid. The chlorine liberated was absorbed in potassium iodide solution and the iodine thus set free titrated against standard thiosulphate. The total manganese was determined by the pyrophosphate method. The product was found to conform to the formula $MnO_{1·97}$ and its susceptibility was found to be $29·00 \times 10^{-6}$ at $20°$. Literature, however, reports divergent values varying between $27·00$ and $46·58 \times 10^{-6}$ for the dioxide (Meyer, *Wied. Ann.*, 1899, **68**, 325; **69**, 236; *Ann. Physik*, 1900, **1**, 664 ; Wistrand, " Magnetiska Susceptibilitaten hos Kvarts etc." Upsala 1916 ; Wedekind and Horst, *Ber.*, 1915, **48**, 105). These values have been more fully discussed in a separate communication which will shortly be published.

Ferric Oxide.—The hydroxide was precipitated by adding ammonia to ferric chloride and the product dehydrated at $500°$ in an electric furnace. (Found: Fe, $69·8\%$; calc. $70·0\%$). The observed susceptibility for the oxide was $21·00 \times 10^{-6}$ at $20°$ (cf. $\chi_{Fe_2O_3} = 20·6 \times 10^{-6}$ at $18°$, International Critical Tables).

The susceptibility of an intimate mixture of potassium chlorate and the catalyst approximately in the ratio of $4 : 1$, was determined after analysis. It was then heated at different temperatures (below the temperature of spontaneous ignition) for different intervals of time, its χ determined and the products analysed at each stage. The methods of analyses are given below.

Chloride and Chlorate.—The mixture was treated with water till free of chloride and chlorate and the filtrate made up to known volume. Chloride was estimated by Volhard's method and the chlorate was reduced to chloride in an aliquot portion with sulphur dioxide and the chloride determined as above.

Analyses.

Manganese was estimated by the pyrophosphate method and the active oxygen determined in the insoluble residue iodometrically.

Ferric oxide was estimated by precipitation as hydroxide followed by ignition to Fe_2O_3.

The results, so obtained, are set forth in Tables I and II, the χ-value in each case representing the mean of at least three observations.

Since the composition of the mixture and the susceptibility of its components at various stages are known, the theoretical value of χ is that arrived at on the additivity law for a mixture.

TABLE I.

Catalytic decomposition of potassium chlorate with manganese dioxide.

$$\chi_{MnO_2} = 29 \cdot 00 \times 10^{-6}$$

$$\chi_{KCl} = -0 \cdot 516 \times 10^{-6}$$

$$\chi_{KClO_3} = -0 \cdot 300 \times 10^{-6}$$

MIXTURE I.

Reading.	Temp. heating	Time.	Composition of the solid residue				$\chi \times 10^6$		Diff. $(a-b)$
			MnO_2.	$KClO_3$.	KCl.	Total.	Exp. (a)	Calc. (b)	$\times 10^6$.
1	..	...	18·80%	81·06%	0·00%	99·86%	5·20	5·21	−0·01
2	250-260°C	0·5 hr.	19·71	76·92	3·25	99·88	5·23	5·47	−0·24
3	270-280°	1·0	21·10	58·49	20·25	99·84	5·59	5·84	−0·25
4	290-300°	1·0	22·75	42·01	35·12	99·88	6·03	6·29	−0·26
5	300-310°	1·0	25·10	23·89	51·00	99·99	6·69	6·94	−0·25
6	320-330°	Spontaneous	27·20	0·00	72·63	99·83	7·53	7·51	+0·02

MIXTURE II.

1	...	..	18·80	81·06	0·00	99·86	5·20	5·21	−0·01
2	250-260°	0·5	19·68	77·05	3·16	99·89	5·21	5·46	−0·25
3	270-280°	1·0	21·13	58·41	20·31	99·85	5·58	5·85	−0·27
4	290-300°	1·0	22·76	42·03	35·21	100·00	6·05	6·30	−0·25
5	300-310°	1·0	25·03	23·86	51·03	99 92	6·69	6·92	−0·23
6	320-330°	Spontaneous	27·22	0·00	72·65	99·87	7·51	7·52	−0·01

TABLE II.

Catalytic decomposition of potassium chlorate with ferric oxide.

$$\chi_{Fe_2O_3} = 21 \cdot 00 \times 10^{-6}.$$

MIXTURE I.

Read-ing.	Temp.	Time.	Composition of the solid residue			Total.	$\chi \times 10^6$ Exp. (a)	$\chi \times 10^6$ Calc. (b)	Diff. $(a-b) \times 10^6$.
I	...	...	20·45%	79·35%	0·00%	99·80%	4·05	4·06	−0·01
2	250-260°	0·5 hrs.	21·00	75·03	3·73	99·76	4·19	4·17	+0·02
3	290-300°	1·0	22·13	64·47	13·17	99·77	4·36	4·39	−0·03
4	300-310°	1·0	23·85	50·20	25·51	99·56	4·70	4·73	−0·03
5	310-320°	1·0	26·30	23·51	50·03	99·84	5·19	5·19	−0·00
6	340-350°	Sponta-neous	29·40	0·00	70·33	99·73	5·82	5·81	+0·01

MIXTURE II.

I	...	...	20·45	79·35	0·00	99·80	4·05	4·06	−0·01
2	250-260°	0·5	20·95	75·15	3·65	99·75	4·17	4·16	+0·01
3	290-300°	1·0	22·20	64·24	13·36	99·80	4·40	4·40	0·00
4	300-310°	1·0	23·90	50·11	25·73	99·74	4·71	4·74	−0·03
5	310-320°	1·0	26·33	23·60	50·13	100·06	5·18	5·20	−0·02
6	340-350°	Sponta-neous	29·43	0·00	70·29	99·72	5·82	5·82	0·00

DISCUSSION.

The numerous theories which have been advanced from time to time in order to explain the reaction mechanism of the catalysed decomposition with manganese dioxide are essentially (a) mechanical, and (b) chemical in nature.

The mechanical hypothesis has been dealt with earlier (*vide supra*). While studying the catalytic decomposition of potassium chlorate by oxides and metals Psarshevski (*Sci. Mag. Chem. Cath. Katerinoslav,* 1926, p. 165) remarked that their action is due to a mechanical disturbance of the equiii-brium of the electrons of the chlorate molecule. It is ˙supposed that the

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absorbed gases are ionised by the impact of electrons of the catalyst and thereafter act upon the salt. The magnetic results, however, leave no doubt about the formation of an intermediate compound and hence it appears that manganese dioxide actively takes part in the kinetics of the reaction. Any chemical explanation must be of the nature of a cycle of changes which ultimately result in the release of the dioxide.

It is to be noted that the observed paramagnetic susceptibility of the reaction mixtures (*vide* Table I) at the intermediate stages is lower than the value calculated on the mixture law and consequently the alleged inter-mediate compound must be either diamagnetic or at least less strongly para-magnetic than the original dioxide.

Wachter's hypothesis which postulates the development of manganous salts as intermediate compounds consequently involves an increase in paramagnetism, since on the Bose-Stoner formula

$$\sqrt{\mu_B} = 4S(S+1),$$

Mn$^{..}$ and Mn$^{...}$ ions have magnetic moments of 5·92 and 3·87 Bohr units respectively is therefore ruled out.

The evolution of traces of chlorine which accompany these changes, however, led McLeod to propose the following scheme of reaction:

$$2KClO_3 + 2MnO_2 \longrightarrow 2KMnO_4 + Cl_2 + O_2$$

the permanganate next breaks up according to the equation,
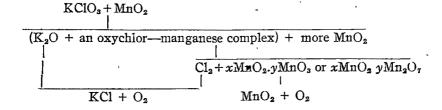
$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

and ultimately this is followed by

$$K_2MnO_4 + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2.$$

In this scheme the liberation of free chlorine necessitates the formation of an equivalent amount of potassium oxide or possibly permanganate or manganate in the free state. The observed deviation of susceptibility from the calculated values as recorded in Table I should *a priori* be due to the formation of one or more of these compounds, and since on McLeod's mechanism these compounds are progressively formed with increased evolu-tion of free chlorine at every stage, the observed susceptibility values ought to show a continuous decrease all through, the maximum differences being obtained at the final stage. This is contrary to the present observations. Moreover, the amount of potassium permanganate or oxide that can be formed equivalent to the chlorine actually liberated, is totally inadequate to account for the marked lowering of susceptibility observed here, its contribu-tion being barely to the extent of 0·01—0·02 × 10^{-6}, whereas the observed difference is in the neighbourhood of 0·25 × 10^{-6}

Deniges (*Bull. trav. Soc. Pharm. Bordeaux*, 1936, 74, 93) has shown from spectroscopic evidence that MnO_4 ion is developed in the course of this reaction but he definitely precludes the possibility of potassium permanganate formation, since $KMnO_4$ was found to exercise no catalytic influence on the decomposition. He, however, holds manganese permanganate that may have beeen formed in course of the reaction responsible for the accelerated reaction velocity. It is, however, by no means certain that manganous permanganate is actually developed in the reaction. Magnetic considerations, in fact, seem to invalidate its formation. Although theoretically on the Bose-Stoner formula, manganous permanganate should be less strongly paramagnetic than manganese dioxide containing quadrivalent manganese $\{\chi_{Mn(MnO_4)_2} = 4940 \times 10^{-6}$ and $\chi_{MnO_2} = 6350 \times 10^{-6}\}$, yet it is well known that the magnetic behaviour of MnO_2 deviates widely from the theoretical and the deviation is towards lesser paramagnetism $\{\chi_{MnO_2}$ (Exptl.) $= 2520 \times 10^{-6}\}$. The formation of $Mn(MnO_4)_2$ will, in consequence, produce greater paramagnetism than the calculated values indicate at the intervening stages of the reaction.

The following scheme, which involves the separation of potassium and chlorine, through the formation of a complex, possibly of the Werner type, is tentatively suggested.

$$KClO_3 + MnO_2$$

$$(K_2O + \text{an oxychlor—manganese complex}) + \text{more } MnO_2$$

$$Cl_2 + xMnO_2.yMnO_3 \text{ or } xMnO_2\,yMn_2O_7$$

$$KCl + O_2 \qquad MnO_2 + O_2$$

The formation of these complexes readily explains the magnetic results. On theory, hepta- or hexa-valency of manganese will obviously result in lowering of paramagnetic susceptibility. The formation of $MnO_4^-,-$ as observed spectroscopically by Deniges (*loc. cit.*) and of the different oxides of manganese the formation and breaking up of which according to Sodeau are responsible for the catalytic activity, follow as the direct consequence of the side-reaction in this cycle.

In the case of the reaction catalysed by Fe_2O_3, close concordance is obtained between the observed and the calculated values of χ as recorded in Table II. The reaction may involve electronic disturbances of the type proposed by Psarshevski (*loc. cit.*) in which the activation energy supplied by the catalyst molecule is regained by it after the chlorate molecule has

undergone dissociation. Fowler and Grant (*Trans. Chem. Soc.*, 1890, 57, 277) conclude from the close agreement of its mode of action with that of manganese dioxide that an analogous reaction takes place, involving the formation of intermediate products. If this is so, the intermediate compound so formed must be very unstable, since no deviations from the mixture law have been observed though the possibility of a relatively stable intermediary, which may result in the mixture having the same susceptibility all through, should not be precluded.

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MAGNETISM AND CATALYSIS. PART II. CATALYSIS OF PERSULPHATE AND IODIDE REACTION BY FERROUS IONS.

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Magnetic evidence is adduced in regard to the formation of a relatively stable intermediate compound which is responsible for the accelerated velocity of the iodide-persulphate reaction. The reaction obviously does not take place merely *via* the formation of ferric sulphate which has been the view so far. The nature of the compound is discussed.

Recently the mechanism of the catalytic reaction between persulphate and iodide has elicited some controversy. Calculations based on the measurements of reaction velocity in the presence of $Fe^{..}$ ions led Kiss and Zombory (*Rec. trav. chim.*, 1927, **46**, 225) to express the reaction as follows:—

$$2Fe^{..} + S_2O_8^{--} \longrightarrow 2Fe^{...} + 2SO_4^{--}$$

$$2Fe^{...} + 2I' \longrightarrow 2Fe^{..} + I_2$$

Saal (*ibid.*, 1928, **47**, 385), while studying the velocity of ionic reactions observed that the amount of iodine formed by catalysis, as calculated from the coefficient of these reactions, is not compatible with the observed value and hence concluded that the catalytic influence cannot be wholly explained by these reactions. Kiss (*ibid.*, 1929, **48**, 508) accumulated new data in support of his earlier interpretation. The mechanism of oxidation has lately been studied by Afanasiev (*J. Phys. Chem. Russ.*, 1937, **9**, 559) who has emphasised the specificity of the action of $Fe^{..}$ ions.

The present investigation is concerned with the clarification of the reaction mechanism from magnetic standpoint.

EXPERIMENTAL.

The purity of the substances employed was of a very high order. B. D. H. analytical reagents were purified and qualitatively and quantitatively analysed before use.

In the case of solutions, susceptibility has been calculated with the help of the reaction :

$$\chi_{soln} = \chi_{salt} \times C_{salt} + \chi_{solvent} (1 - C_{salt}).$$

Specific susceptibilities of the solutions of the same order of strength as were to be used in the reaction, were also determined and this relationship found to be valid.

The following solutions were prepared in conductivity water of which the susceptibiiity had been previously determined :

(a) 0·10N-Potassium iodide.
(b) 0·05N-Potassium persulphate
(c) 1·00% Ferrous sulphate.

The solutions were placed in a constant temperature bath at 20°. After they had attained the temperature of the bath, 100 c.c. each of the iodide and persulphate solutions were pipetted out in a dry glass-stoppered flask and immediately shaken. Initial time was taken and the progress of the reaction followed by a chemical and magnetic analysis of the mixture at different intervals of time. The chemical composition was determined by withdrawing a known volume of the mixture, arresting the reaction in ice and immediately titrating the iodine set free against standard thiosulphate. The composition of the mixture with respect to its other ingredients can easily be evaluated from the thiosulphate consumption, since the latter is an accurate measure of the iodine content.

The specific susceptibilities of the reaction mixture were measured at different intervals and knowing the composition by a reference to the graph (time—thiosulphate), the values calculated theoretically on the mixture law were compared with the experimental values. These results are embodied in Tables IA and IB.

The reaction was next studied under exactly identical conditions in the presence of the catalyst. In this case 99·0 c.c. of 0·101N-potassium iodide were first measured out in the flask, 1 c.c. of the catalyst solution added and 100 c.c. of 0·05 N-persulphate mixed last of all. The reaction mixture was analysed chemically at different stages as above and its susceptibility determined on the Gouy's balance. The results of these measurements are embodied in Tables II A and II B.

The theoretical values of χ were calculated on the following data.

Compound.	$-\chi \times 10^6$.	Compound.	$-\chi \times 10^6$.
Iodine	+0·36	K_2SO_4	+0·403
$K_2S_2O_8$	+0·371	KI	+0·422
		$FeSO_4,7H_2O$	−41·5

Reaction without catalyst.

TABLE IA.

Chemical analysis.

Vol. of the mixture solution used for tirration $= 10$ c.c. Strength of thiosulphate $= N/51 \cdot 75$. Temperature $= 20°$. V denotes volume of thio.

Reading.	Time.	V.	Reading.	Time.	V.
1	4 min.	0·40 c.c.	9	180 min.	7·70 c.c.
2	26	2·15	10	235	8·45
3	50	3·65	11	275	8·85
4	66	4·50	12	310	9·10
5	82	5·10	13	345	9·25
6	102	5·85	14	396	9·45
7	125	6·55	15	460	9·60
8	155	7·25			

TABLE IB.

Magnetic analysis.

d_4^{20} of the solution $= 1 \cdot 009$. χ of water $= -0 \cdot 730 \times 10^{-6}$.

Reading.	Time.	Thio used.	Percentage composition.				$-\chi \times 10^6$	
			KI.	$K_2S_2O_8$.	K_2SO_4.	I_2.	Expt.	Calc.
1	23 min.	2·10 c.c.	0·7627	0·2830	0·0707	0·0515	0·726	0·726
2	46	3·60	0·7147	0·2439	0·1212	0·0883	0·726	0·726
3	62	4·46	0·6871	0·2214	0·1502	0·1094	0·727	0·726
4	78	5·05	0·6681	0·2059	0·1701	0·1239	0·727	0·726
5	100	5·80	0·6440	0·1864	0·1954	0·1423	0·727	0·726
6	122	6·50	0·6216	0·1681	0·2189	0·1594	0·727	0·726
7	150	7·20	0·5991	0·1498	0·2425	0·1766	0·727	0·726
8	177	7·65	0·5846	0·1380	0·2577	0·1877	0·727	0·726
9	247	8·55	0·5558	0·1145	0·2879	0·2097	0·727	0·726
10	270	8·82	0·5470	0·1074	0·2972	0·2164	0·727	0·726
11	303	9·04	0·5400	0·1017	0·3045	0·2218	0·727	0·726
12	340	9·22	0·5342	0·0970	0·3106	0·2262	0·727	0·726
13	408	9·46	0·5265	0·0907	0·3187	0·2321	0·728	0·726
14	456	9·60	0·5221	0·0871	0·3233	0·2355	0·728	0·726

Reaction with catalyst.

TABLE IIA.

Chemical analysis.

Reading.	Time.	Vol. of $N/51.50$ thiosulphate	Reading.	Time.	Vol. of $N/51.50$ thiosulphate.
1	5 min.	0·95 c.c.	7	95 min.	7·35 c.c.
2	15	2·25	8	112	7·95
3	27	3·50	9	126	8·30
4	46	4·90	10	166	9·10
5	62	5·95	11	204	9·65
6	76	6·60	12	6 hrs.	11·00

TABLE IIB.

Magnetic analysis.

d_4^{20} of the solution $= 1.009$. χ of water $= -0.730 \times 10^{-6}$.

Reading.	Time.	Thio used.	Percentage composition.					$-\chi \times 10^6$.	
			KI.	$K_2S_2O_8$.	K_2SO_4.	I_2.	$FeSO_4$, $7H_2O$.	Expt.	Calc.
1	12 min.	2·00 c.c.	0·7656	0·2854	0·0677	0·0493	0·005	0·724	0·724
2	25	3·00	0·7334	0·2592	0 1015	0·0739	b·005	0·727	0·724
3	44	4·80	0·6754	8·2119	0·1625	0·1183	0·005	0·730	0·724
4	60	5·80	0·6431	0·1856	0·1963	0·1430	0·005	0·733	0·724
5	75	6·54	0·6193	0·1662	0·2213	0·1612	0·005	0·730	0·724
6	92	7·30	0·5948	0·1463	0·2471	0·1799	0·005	0·728	0·724
7	110	7·90	0·5754	0·1305	0·2674	0·1947	0·005	0·726	0·724
8	126	8·30	0·5625	0·1200	0·2809	0·2046	0·005	0·724	0·724
9	166	9·10	0·5367	0·0990	0·3080	0·2243	0·005	0·723	0·724
10	200	9·60	0·5206	0·0859	0·3248	0 2366	0·005	0·723	0·724
11	6 hr.	11·00	0·4754	0·0491	0·3724	0·2712	0·005	0·723	0·724

DISCUSSION.

It is clear from Table IB that in the case of uncatalysed reaction, the observed susceptibilities follow, more or less, the additivity rule for a mixture. This shows that the formation of the iodide-iodine complex, KI·I₃

in the reaction may have only a slight influence on the susceptibility (*cf.* Bhatnagar, Kapur and Varma, *Indian J. Phys.*, 1934, **9**, 131 ; Ranganadham, *ibid.*, 1931, **6**, 421).

In case of the catalysed reaction, the magnetic data (Table II B) reveal that

(*a*) at the initial stage, the mixture law is obeyed ;

(*b*) at intermediate stages, there is a marked divergence from it and the trend of values is towards greater diamagnetism ;

(*c*) at the final stages, divergence is but slight. This clearly indicates the formation of a relatively stable intermediary which is responsible for the accelerated velocity of the reaction. If iodine is liberated merely *via* ferric sulphate, as has been suggested by Kiss and Zombory (*loc. cit.*), the susceptibility of the resulting solutions ought to have remained more or less unchanged or at any rate the trend of values should have been towards lesser diamagnetism. (The ionic susceptibilities for $Fe^{..}$ and $Fe^{...}$, calculated from the observed values for $FeSO_4$ and $Fe_2(SO_4)_3$ are $\chi_{Fe^{..}} = 11237 \times 10^{-6}$ and $\chi_{Fe^{...}} = 11405 \times 10^{-6}$).

This is contrary to observations and hence it appears that the reaction mechanism involves the formation of a relatively stable diamagnetic or feebly paramagnetic complex, but it is abundantly clear that the mere formation of ferric sulphate cannot wholly account for the accelerated reaction velocity. The reaction mechanism may possibly entail the formation of a six-fold complex co-ordination compound of ferrous ion, since such a compound will have zero magnetic moment (Bose, *Phil. Mag.*, 1928, **5**, 1048 ; Welo and Baudisch, *Nature*, 1925, **116**, 606), as for example in the case of potassium ferrocyanide. Though it is not possible to say purely from magnetic considerations as to what compound is actually developed in the reaction, yet the importance of this method lies in the fact that it throws doubt on the earlier concepts of the mechanism of this reaction and indicates the direction in which to look for a proper interpretation for which further work is in hand.

PYRONES AND RELATED COMPOUNDS. PART I FORMA-TION AND STRUCTURE OF 2:6-DIHYDROXY-1:4-PYRONE.

By R. Kaushal.

2:6-Dihydroxy-1:4-pyrone has been obtained from acetone dicarboxylic acid and its various derivatives have been described.

Pechmann and Neger (*Annalen*, 1893, **273**, 186) found that the action of acetic anhydride on acetone dicarboxylic acid is unusual as the reagent acetylates the acid at the carbon instead of at the hydroxylic oxygen yielding the acetylated product (I), which immediately changes to dehydro-acetocarboxylic acid (II).

$$ \text{(I)} \qquad\qquad \text{(II)} $$

According to them if purified acetone dicarboxylic acid is used in place of the crude one containing sulphuric acid, the yield of (II) is much decreased.

By shaking pure acetone dicarboxylic acid (free from sulphuric acid) with acetic anhydride Willstätter and Pfannenstein (*Annalen*, 1921, **422**, 7) obtained the anhydride (III) of acetone dicarboxylic acid having the same melting point as the acid namely 137°.

$$ \text{(III)} \qquad\qquad \text{(IV)} \qquad\qquad \text{(V)} $$

Willstätter's experiment was repeated and it was found that at comparatively low temperature (about 20°), the anhydride (III) is formed but at room temperature (about 30°) a new substance is produced which melted at 94° and which is found to be an isomer of (III). The isomer differs from the anhydride in the following respects :—

(i) The anhydride readily dissolves in water to form the acid while the isomer is stable and could be crystallised from hot water.

(ii) It dissolves in cold alkalis from which it is recovered unchanged on quickly acidifying. But with hot aqueous alkali it is decomposed.

(iii) It can be crystallised from hot alcohol with which the anhydride forms the acid-ester of acetone dicarboxylic acid.

(iv) It forms a nitrophenylhydrazone melting at 215°, while the anhydride does not. Acetone dicarboxylic acid, however, forms a nitrophenylhydrazone melting at 153°.

The anhydride changes into the isomer in contact with hot acetic anhydride, while in contact with aqueous hydrochloric acid or sulphuric acid the isomer changes gradually into the acetone dicarboxylic acid, the presence of which is confirmed by the formation of addition product with boiling mercuric sulphate solution (Deniges, *Compt. rend.*, 1898, **128**, 680). The change of the isomer into the acid is not instantaneous and obviously takes place *via* the anhydride.

The isomer, therefore, is 2:6-dihydroxy-1:4-pyrone (IV, R=OH). Like pyrones it forms a crystalline addition product with mercuric chloride but does not form a chloroplatinate or a picrate, probably because in the formation of these, hydrochloric acid is necessary in contact with which it changes into acetone dicarboxylic acid. It reacts with *p*-nitrophenylhydrazine which justifies the ketonic structure.

With methyl alcoholic ammonia at 0°, it forms the di-ammonium compound of 2:6-hydroxy-4-pyridone (V), which is being investigated further and will form part of a later communication.

With two molecules of phosphorus pentachloride the hydrochloride of 2:6-dichloropyrone results melting at 105°, from which by neutralising the hydrochloric acid the dichloropyrone (IV, R=Cl) is obtained.

With sodium ethylate in alcoholic solution a disodium compound (IV, R=ONa) is formed.

From the disodium compound and ethyl iodide in alcohol, 2:6-diethoxy-pyrone (IV, R=OEt) is produced. It is a pleasant smelling liquid, b.p. 65-68°/6 mm., which forms a crystalline addition product with mercuric chloride.

Acetyl chloride and acetic anhydride in the presence of a trace of sulphuric acid do not acetylate the dihydroxypyrone but produce dehydroacetocarboxylic acid (II). Nevertheless, from the disodium compound of the pyrone and 3:5-dinitrobenzoyl chloride· in boiling benzene the dinitrobenzoate [IV, $R=C_6H_3(NO_2)_2$-CO-O], m.p. 90°, is produced.

Attempts to obtain a diphenylurethane resulted in the formation of diphenylurea, a tendency shown by most of the tertiary alcoholic compounds.

E X P E R I M E N T A L.

Preparation of Acetone dicarboxylic Anhydride (III).—To well-cooled acetic anhydride (8 g.) purified acetone dicarboxylic acid (4 g.) was added and the mixture was shaken, temperature being not allowed to rise above 20°. The acid went into solution and on keeping for $\frac{1}{4}$ hour in ice and shaking, the anhydride separated as prisms. It was filtered, washed with benzene and dried, m.p. 136-37° (decomp.) changing to a red liquid, yield 2 g.

2:6-Dihydroxy-4-pyrone (IV, R=OH). Acetone dicarboxylic acid ·(50 g.), freed from sulphuric acid by crystallisation from acetic acid, was shaken at room temperature (30°) with acetic anhydride (100 g.) until the acid went into solution with slight evolution of heat. The solution was · allowed to remain overnight, when the dihydroxypyrone separated in shining plates and the colour· had changed to red. ·It was filtered and washed with benzene. The filtrate on standing gave a second crop of the pyrone, total yield of the crude product is 28 g. It crystallises from benzene in long shining needles, m.p. 94°. [Found: C, 47·2; H, 3·7. M.W., (by titration)', 128·4. $C_5H_4O_4$ requires C, 46·8; H, 3·1 per cent. M.W., 128]. It develops a violet colour with ferric chloride.

The *nitrophenylhydrazone* separated as a yellow solid on mixing the dihydroxypyrone and *p*-nitrophenylhydrazine, separately dissolved in 50% acetic acid. It was filtered and washed with dilute acetic acid and crystallised from pyridine, m.p. 215°. (Found: N, 16·6. $C_{11}H_9O_5N_3$ requires N, 16·0 per cent).

The *mercuric chloride addition product* was obtained as a crystalline solid by mixing equivalent quantities of mercuric chloride and dihydroxypyrone separately dissolved in ether and on evaporation of the solvent. It crystallised from water, m.p. 235° (decomp.). (Found: Hg, 50·8. $C_5H_4O_4$, $HgCl_2$ requires Hg, 50·2 per cent).

Conversion of Acetone dicarboxylic Anhydride into Dihydroxypyrone.—The anhydride (0·5 g.) was dissolved in acetic anhydride (1 g.) on

warming and left overnight. Next day on rubbing the pyrone separated in shining needles, yield 0·4 g. It was crystallised from benzene in shining needles, m.p. and mixed m.p. with a genuine sample of the dihydroxypyrone 94°.

Conversion of Dihydroxypyrone into Acetone dicarboxylic Acid.— The dihydroxypyrone was left in contact with a trace of hydrochloric acid when it went into solution. The resulting solution on pouring into boiling aqueous mercuric sulphate gave a white crystalline product, which proved to be identical with the addition product 2 Hg $C_5H_4O_5$, $HgSO_4$, 2 HgO. The addition product is insoluble in water and soluble in dilute hydrochloric acid. The presence of sulphuric acid, however, does not interfere in its formation.

Di-ammonium salt of 2 : 6-Dihydroxy-4-pyridone.—The dihydroxypyrone (2 g.) was added to well-cooled saturated methyl alcoholic ammonia (15 c.c.), and the solution was kept in ice for 2 hours when the ammonium compound separated as clusters of needles. It was filtered, washed with methyl alcohol and dried on a porous plate, m.p. 97° with sintering at 92°, yield almost quantitative. It is very hygroscopic and it gives a violet colour with aqueous ferric chloride. It is very soluble in water and dilute hydrochloric acid. With cold caustic soda it evolves ammonia. (Found : N, 22·2. $C_5H_5O_3N$, 2NH_3, CH_3OH requires N, 21·76 per cent) A similar compound, *viz.*, ammonium salt of 2 : 6-dihydroxy-4-pyridone semicarbazone has been recently described by Jacini (*Gazzetta*, 1937, **67**, 715).

Hydrochloride of Dichloropyrone was prepared from dihydroxypyrone (4·5 g., 1 mol.) and phosphorus pentachloride (15 g., 2 mol.). After keeping in boiling water for 5 minutes the reaction mixture was added to water when a paste was obtained which on extraction with boiling water and cooling deposited the dichloropyrone hydrochloride in thin silky plates, m.p. 103-4°, yield 1·2 g. If, however, the liquid after the reaction was distilled under reduced pressure after removing phosphorus oxychloride, it distilled at 110-130°/4 mm. with much decomposition, and it gradually solidified to colourless needles. Probably the hydrochloride during distillation dissociates into the dichloropyrone and hydrochloric acid.

The hydrochloride crystallises from benzene in colourless needles, m.p. 105°. [Found : C, 30·6 ; H, 1·7 ; Cl, 53·4; M.W. (by titration). 196. $C_5H_2O_2Cl_2$, HCl requires C, 29·8, H, 1·5 ; Cl, 52·8 per cent. M.W., 201·5 for monobasic].

2 : 6-*Dichloro-4-pyrone* (IV, R=Cl) was obtained from the hydrochloride by neutralising an alcoholic solution with 2N-caustic soda. The solution

was evaporated nearly to dryness at room temperature and the dichloro-pyrone was extracted with ethyl acetate. It crystallises as thick needles, m.p. 78-80°. (Found : Cl, 43˙2. $C_5H_2O_2Cl_2$ requires Cl, 43˙0 per cent).

Disodium compound of dihydroxypyrone was obtained by adding sodium ethylate prepared from 0˙5 g. (2 atoms) of sodium with dihydroxy-prone (1˙3 g., 1 mol.) in absolute alcohol. The sodium salt separating was filtered, washed with alcohol and finally with ether, yield 1˙8 g (Found in the compound dried at 120° for 6 hours : Na, 27˙4. $C_5H_2O_4Na_2$ requires Na, 26˙7 per cent).

2:6-*Diethoxypyrone* (IV, $R = OC_2H_5$).—To the suspension of the sodium derivative of dihydroxypyrone, prepared from 0˙92 g. (2 atoms) of sodium to 2˙5 g. (1 mol.) of dihydroxypyrone, dissolved in alcohol, ethyl iodide (7 g.) was added and the mixture refluxed on a water-bath for 8 hours with the addition of more ethyl iodide (2 g.). On distilling off the alcohol and acidification, the oil was extracted with ether, the ethereal extract was washed with dilute alkali and water, dried over calcium chloride and ether distilled. It distilled at 65-70°/6 mm., yield 1˙5 g. (Found : C, 59˙0 ; H, 6˙6. $C_9H_{12}O_4$ requires C, 58˙7 ; H, 6˙6 per cent). The diethoxy compound is a colourless liquid with a pleasant camphor-like odour. It does not form a chloroplatinate or a picrate and it is insoluble in hydrochloric acid. In ethereal solution it forms an addition product with mercuric chloride, which was crystallised from water by evaporation of the solvent, m.p. 265° (decomp.).

Action of Acetyl Chloride and Acetic Anhydride on Dihydroxypyrone.— The dihydroxypyrone was heated with the reagents in presence of a few drops of sulphuric acid and the reaction mixture on pouring into water gave shining plates, m.p. 154°. It was identified to be dehydroacetocarboxylic acid by mixed m.p. and the formation of the potassium derivative.

Di-3 : 5-dinitrobenzoate of the dihydroxypyrone was obtained by reflux-ing on a water-bath for 8 hours the suspension of the sodium compound of the pyrone (1 mol.) in dry benzene and 3 : 5-dinitrobenzoyl chloride (2 mols). It was filtered and the filtrate deposited crystals. They were collected and washed with ether and then with alcohol. It crystallised from benzene-alcohol as needles, m.p. 90°. From 2 g. of the sodium compound 0˙5 g. of the pure substance was obtained. (Found : C, 43˙7; H, 1˙4 ; N, 11˙3. $C_{19}H_8O_{14}N_4$ requires C, 44˙1 ; H, 1˙55 ; N, 10˙85 per cent).

Action of Phenylisocyanate on Dihydroxypyrone.—Equivalent quantities of the dihydroxypyrone and phenylisocyanate were mixed and the mixture gently heated for 10 minutes. On cooling a solid was obtained which was

filtered, washed with dilute caustic soda and finally crystallised from 90% alcohol as almost colourless prisms, m.p. 236-37°. (Found : N, 13·0 per cent). This proved to be diphenylurea, m.p. 238°.

The author wishes to express his gratefulness to Prof. S. S. Deshapande for his kind interest in the work.

REVIEW

The Elements of Physico-Pharmaceutical Calculations.—By Prof. M. L. Schroff. Published by the U. P. Pharmaceutical Association, 1940 ; Benares Hindu University, Pp. 281.

The book is intended for junior students acquainted with the fundamental theories of chemistry. The treatment is very lucid. The author has spared no pains to explain the simple physical principles underlying chemical analysis by working out numerous well-selected examples. The chapters on electrochemistry and oxidation-reduction potentials are well written. The discussion on significant figures in the opening chapter is welcome, and is hoped to be read with profit by those for whom it is intended.

The tenth chapter contains a short treatment on calculations most frequently used in oil analysis. Similar calculations required in the analysis of various biochemical substances could be incorporated in this book on pharmaceutical calculations. The chapter on indicators could be improved upon by discussing indicators other than methyl orange and phenolphthalein —both single and mixed,—and their application in biochemical analysis.

J. G.

STUDIES IN THE NAPHTHALENE SERIES. PART I. SYNTHESIS OF 1-KETO-5-BROMO (OR CHLORO-)-7:8-DIMETHOXY-1:2:3:4-TETRAHYDRONAPHTHALENE.

BY RAFAT HUSAIN SIDDIQUI.

1-Keto-5-bromo-7:8-dimethoxy-1:2:3:4-tetrahydronaphthalene and 1-keto-5-chloro-7:8-dimethoxy-1:2:3:4-tetrahydronaphthalene have been prepared   The ketones give their characteristic derivatives.

The object of the present synthesis was to synthesise some of the preliminary degradation products of thebaine in order to confirm the statements by different workers (*Annaien*, 1924, **438**, 34; *J. Chem. Soc.*, 1923, **123**, 988; 1926, 2562). For this purpose the synthesis of 3 : 4-dimethoxy-β-ethyloctahydrophenanthrene was contemplated. This work is interrupted for want of facilities and so a brief note embodies the results so far achieved (*Abstract of Dissertations, Oxford University*, 1938, Vol. X). β- : 4-Dimethoxybenzoylpropionic acid and γ-3 : 4-dimethoxyphenyibutyric acid have been obtained in good yield according to the method of Haworth and Mavin (*J. Chem. Soc.*, 1932, 160). The latter gives a quantitative yield of γ-6-bromo-3 : 4-dimethoxyphenylbutyric acid. This gives 1-keto-5-bromo-7 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene in 10-15% yield on treatment with phosphorus pentoxide. The use of the related chloro-acid improves the yield of the ketone (35%). The optimum conditions for the reaction have yet to be found.

β-3 : 4-Dimethoxybenzoylpropionic acid was prepared according to the method of Haworth and Mavin (*loc. cit.*) and crystallised from dilute acetic acid in prisms, m.p. 160-61° (*cf.* Haq, Kapur and Ray, *J. Chem. Soc.*, 1933, 1088, who give m.p. 165°). This acid on Clemmensen reduction gave an oily product, which on rubbing and standing after the solution had been diluted with water, separated in slightly coloured beads and after distillation was recrystallised from dilute acetic acid at 0° in white shining prisms, m.p. 60-61° (m.p. 57-59°, Haworth and Mavin, *loc. cit.*).

γ-6-*Bromo*-3 : 4-*dimethoxyphenylbutyric   Acid.*—The preceding acid (46·5 g., 1 mol.) was dissolved in acetic acid and bromine vapour (11·18 g., 1 mol.) diluted with dry air was passed through the solution when the bromo-

acid separated in prisms. On recrystallisation from acetone it melted at 139-40° (m.p. 135-36°, Haworth and Mavin). It is soluble in acetone, ethyl acetate, benzene, alcohol, less so in ether and insoluble in petroleum ether. It suffered no loss in weight on drying at 100° in *vacuo*. (Found: C, 47·1 ; H, 5·0 ; Br, 25·4 ; OMe, 18·5. Calc. for $C_{12}H_{15}O_4Br$: C, 47·5; H, 5·1; Br, 26·4; OMe, 20·5 per cent).

1-*Keto-5-bromo-7 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene.*—The preceding acid (5 g.) was dissolved in moist benzene (500 c.c.) and to the gently boiling solution phosphorus pentoxide (50 g.) was added in four instalments during 1½ hour. The solution, after refluxing for further ½ hour, was cooled and the mixture decomposed by adding ice to the solution at 0°. It was then made alkaline with sodium hydroxide and extracted with benzene. The dark oily residue (3 g.) from the washed and dried benzene layer was dissolved in alcohol and water added to it when some dark brown slimy product separated which was rejected. The clear solution on slow evaporation gave the ketone in thick crystals in 10-15% yield which after recrystallisation from dilute acetic acid had m.p. 91-92°. In a second experiment an attempt was made to purify the crude ketone (13 g.) by converting it into its semicarbazone but three products were obtained on fractional crystallisation of which the second was perhaps the mixture and the first only was the desired product: (*i*) m.p. 198° (1·8 g.); (*ii*) m.p. 188° (3 g.); (*iii*) m.p. 152-59° (6·5 g.). The last fraction gave values which showed that it was not the required product. (Found in material dried at 100° in *vacuo* : C, 45·4; H, 5·2; N, 7·4. $C_{13}H_{16}O_3N_3Br$ requires C, 45·6; H, 4·7; N, 12·3 per cent). The ketone as isolated above after decolourising with charcoal from its methyl alcoholic solution crystallised in perfectly white long thick prisms, m.p. 91-92°. (Found in air-dried material : C, 50·9; H, 4·8; Br, 29·8; OMe, 21·3. $C_{12}H_{13}O_3Br$ requires C, 50·5; H, 4·6; Br, 28·1; OMe, 21·8 per cent). The 2 : 4-*dinitrophenylhydrazone* was obtained in clusters of orange needles, insoluble in alcohol and water, m.p. 220-25° (decomp.). The *semicarbazone* separated in square plates, m.p. 215° after crystallisation from alcohol. (Found: C, 46·2; H, 4·7; N, 11·8. $C_{13}H_{16}O_3N_3Br$ requires C, 45·6; H, 4·7; N, 12·3 per cent).

The semicarbazone (1·7 g.) was hydrolysed by boiling with 20% aqueous oxalic acid solution (4 g. in 20 c.c. of water). After 25 minutes an oil began to separate which on further refluxing became crystalline and melted at 142-43°. It is soluble in sodium carbonate and gives no depression with the bromo-acid on admixture. The semicarbazone (0·5 g.) and oxalic acid (0·5 g.) were refluxed together in acetone solution (50 c.c.) for about 5 hours after which the straw-coloured solution was evaporated.

The residue, after adding water, was shaken three times with ether when unchanged semicarbazone separated from the aqueous solution (0·25 g.). The ether solution was washed with water, dried over anhydrous sodium sulphate and after removal of the solvent gave the bromo-dimethoxytetralone in amber-coloured aggregates of needles, m p. 91-92° and gave no depression on admixture with a pure specimen of the ketone.

γ-6-*Chloro*-3 : 4-*dimethoxyphenylbutyric Acid.*—To a solution of β-3:4-dimethoxyphenylbutyric acid (10 g.), in acetic acid (25 c.c.), chlorine generated from potassium permanganate (5·8 g.) and diluted with carbon dioxide. was ·passed slowly at 0°. The mixture was allowed to stand overnight when the chloro- acid (2·9 g.), m.p. 111-12°, separated in perfectly white needles. A further quantity was obtained from the solution by addition of water (total yield 9·9 g.). The acid was recrystallised from ether-acetone mixture in thick white prisms, m.p. 111-12°. (Found in material dried at 100° in *vacuo* : C, 55·5; H, 6·0; Cl, 13·7; OMe, 25·8. $C_{12}H_{15}O_4Cl$ requires C, 55·6 ; H, 5·8; Cl, 13·7; OMe, 24·0 per cent).

1-*Keto*-5-*chloro*-7 : 8-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene.*— The preceding chloro- acid (10 g.) was dissolved in benzene (800 c.c.) and treated with phosphorus pentoxide (75 g) as in the previous case. The crude ketone was distilled in *vacuo*. The distillate crystallised from an alcohol-ether mixture in prisms and had m.p. 75°, unchanged after crystallisation from methanol (charcoal). (Found in material dried over P_2O_5 : C, 59·1, H, 5·4; Cl, 15·1; OMe, 24·2. $C_{12}H_{13}O_3Cl$ requires C, 59·9; H, 5·4; Cl, 14·8; OMe, 25·8 per cent).

The oxime, prepared in the usual way, crystallised in prisms from methanol in which it is difficultly soluble, m.p. 187°. (Found in material dried at 100° in *vacuo* : C, 56·4 ; H, 5·2; N, 5·4. $C_{12}H_{14}O_3NCl$ requires C, 56·4 ; H, 5·5 ; N, 5·5 per cent). The 2 : 4-*dinitrophenylhydrazone* had m.p. 239-40°.

STUDIES IN THE NAPHTHALENE SERIES. PART II.
SOME REACTIONS OF THE -CH$_2$·CO- GROUP.

By Rafat Husain Siddiqui and Salah-ud-Din.

β-3 :4-Dimethoxybenzoylpropionic acid failed to yield 1 :4 diketone. 1 Keto-6 :7-dimethoxy-1 :2 :3 :4-tetrahydronaphthalene condenses smoothly with aldehydes. Derivatives with aromatic aldehydes are crystalline in most cases but the ketone does not give any *isonitroso* derivative; its benzylidene derivative on oxidation gives *m*-hemipinic acid.

The present investigation has as its object a new synthesis of *m*-hemipinic acid and a study in the rections of the -CH$_2$·CO- group. The problem arose in the attempted synthesis of 3:4-dimethoxy-β-ethyl-octahydrophenanthrene by one of us (R.H.S.). In this connexion 1-keto-5-bromo-7:8-dimethoxy-1:2:3:4-tetrahydronaphthalene has been prepared by cyclising γ-2-bromo-4.5-dimethoxyphenylbutyric acid. This bromo-ketone on oxidation should give a derivative of hemipinic acid but 1-keto-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene, obtained by the ring-closure of γ-3:4-dimethoxyphenylbutyric acid should give *m*-hemipinic acid. Thus the syntheses of two important acids could be effected from one source. In the synthesis of *m*-hemipinic acid it was contemplated that 1:4-diketo-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene and 1-keto-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene would give benzylidene derivatives on condensation with benzaldehyde, which on oxidation would give the desired acid or it could be synthesised by acid hydrolysis of the *isonitroso* derivatives. Attempts to yield 1:4-diketone by cyclising-β-3:4-dimethoxybenzoyl-propionic acid or its ethyl ester in the presence of phosphorus pentoxide, zinc chloride, acetic anhydride, sulphuric acid, etc., have been unsuccessful.

1-Keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene does not give *isonitroso* derivative on treatment with amyl nitrite in presence of acid or alkaline catalysts (*Ber.*, 1901, **34**, 1487 ; 1882, **15**, 1326; 1887, **20**, 2194; 1893, **26**, 241; 1896, **29**, 2605) but it condenses smoothly with aldehydes. The derivatives of acetaldehyde, formaldehyde and crotonaldehyde are all oily liquids and the compounds with aromatic aldehydes are in most cases crystalline products. The following derivatives, 2-benzylidene-, 2-(*o*-,-*m*-, *p*-methoxy)- benzylidene, 2-(3:4-dimethoxy)-benzylidene-, 2-cinnamylidene-, 2-(*o*-, *m*- and *p*-nitro)-benzylidene-2-furfuryl-1-keto-6:7-dimethoxy-tetra-hydronaphthalene, have been prepared and 2-benzylidene derivative has been oxidised with potassium permanganate in neutral solution. The reaction yields an acid, m.p. 174-78° (m.p. of *m*-hemipinic acid 172°,

J. Chem. Soc., 1897, 664; m.p. 195°, *ibid.*, 1901, 400 ; m.p. 1910°; *ibid.*, 1902, 1046, m.p. 175°, *ibid.*, 1910, 1136) in extremely poor yield. The conditions of oxidation in order to improve the yield of the acid are yet to be fixed up ; as we have to stop this work for the present we are publishing the results so far achieved.

EXPERIMENTAL.

Condensation of 1-Keto-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene with Aromatic Aldehydes: 1-Keto-2-benzylidene-6.7-dimethoxy-1:2:3:4-tetrahydronaphthalene.—To a boiling solution of benzaldehyde (6 g.; 1 mol.) in absolute alcohol (125 c.c.) ketone (8·5 g.) was added in portions. On adding potassium hydroxide (2 g. in 10 c.c of water) the solution turned yellow and it was kept simmering on a sand-bath for 2 hours. The solution on cooling yielded benzylidene derivative , m.p.129°, which on recrystallisation from chloroform-alcohol mixture (1:1) was obtained in light yellow silky needles, m.p. 131°. It is soluble in alcohol, acetone, ethyl acetate and readily soluble in chloroform and soluble in petroleum ether. (Found in material dried at 100° in *vacuo*: C, 77·12; H, 6·11. $C_{19}H_{18}O_3$ requires C, 77·55; H, 6·12 per cent).

1-Keto-2-(o-methoxy)-benzylidene-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene.—o-Methoxybenzaldehyde (1·1 g.), alcohol (30 c.c), ketone (1·5 g.) potassium hydroxide (0·5 g. in 2 c.c. of water) were treated as in the previous case and the solution after refluxing and cooling deposited yellow needles, m.p.143°. On recrystallisation from alcohol-chloroform cream-coloured shining needles (m.p.152°) soluble in ethanol, acetone, ethyl acetate and chloroform were obtained. (Found in material dried at 100° in *vacuo*: C, 73·95; H, 6·17. $C_{20}H_{20}O_4$ requires C, 74·07; H, 6·14 per cent).

1-Keto-2-(m-methoxy)-benzylidene -6:7-dimethoxy-1:2: 3: 4 - tetrahydronaphthalene.—The solution of m-methoxybenzaldehyde, ketone and potassium hydroxide in alcohol was refluxed for 2 hours and on dilution with water m-methoxybenzylidene derivative separated as a crystalline mass, m.p. 131°. It was obtained as cream-coloured hexagonal needles, soluble in acetone, chloroform, ethyl acetate and ether on recrystallisation from alcohol-chloroform mixture. (Found in material dried at 100° in *vacuo* : C, 73·49 : H, 6·3. $C_{20}H_{20}O_4$ requires C, 74·07; H, 6·14 per cent).

1-Keto-2-(p-methoxy) -benzylidene-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene.—The above experiment was repeated with *p*-methoxybenzaldehyde and the *p*-methoxybenzylidene derivative was obtained in yellow needles,

m.p., 153°. On repeated crystallisation from alcohol-chloroform it had m.p. 159° and was soluble in the usual organic solvents. (Found in material dried at 100° in *vacuo*: C, 73·7; H,6·27. $C_{20}H_{20}O_4$ requires C, 74·07 ; H, 6·14 per cent).

1-Keto-2-(3:4-dimethoxy)-benzylidene-6:7- dimethoxy-1:2:3:4 -tetrahydro-naphthalene.—Methylvanillin (1·6 g.), alcohol (20 c.c.), ketone (1·8 g.), potassium hydroxide (0·25 g. in 2 c.c. of water) after refluxing gave needles (2 g.), m.p.148°. It was obtained as cream-coloured needles, which crystallised from alcohol-chloroform, m.p. 148°. It is soluble in methanol, ethanol, acetone and ethyl acetate. (Found in material dried at 100° in *vacuo*: C, 70·91; H, 6·14. $C_{21}H_{22}O_5$ requires C, 71·18; H, 6·24 per cent).

1-Keto-2-furfuryl-6.7-dimethoxy-1:2:3:4-tetrahydronaphthalene was obtained from furfuryl aldehyde (0·79 g.), alcohol (20 c.c.), ketone (1·2 g.) potassium hydroxide (0·2 g. in 2 c.c. of water). The red solution after refluxing for 2 hours gave a yellow solid (1·5 g.), soluble in acetone, ethyl acetate, ether and chloroform, m.p. 151°.

1-Keto-2-(3:4-methylenedioxy) - benzylidene-6:7-dimethoxy-1:2:3:4-tetra-hydronaphthalene was obtained by condensing piperonal (1·2 g.) with the ketone (1·5 g.) as light yellow needles (1·4 g.), m.p. 180°, soluble in ethanol, chloroform and acetone. On recrystallisation it had m.p. 182°. (Found in material dried at 100° in *vacuo* : C, 70·63 ; H, 5·43. $C_{20}H_{18}O_5$ requires C, 71·00 ; H, 5·32 per cent).

1-Keto-2-cinnamylidene-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene was obtained in yellow needles, m.p. 155°, soluble in the usual organic solvents. On recrystallisation it had m.p. 160°. (Found in material dried at 100° in *vacuo* : C, 77·30 ; H, 6·26. $C_{21}H_{20}O_3$ requires C, 78·75 ; H, 6·25 per cent. $C_{21}H_{20}O_3$, $\frac{1}{4}$ H_2O requires C, 77·69 ; H, 6·31 per cent).

1-Keto-2-(m-nitro)-benzylidene-6:7-dimethoxy-1:2:3:4-tetrahydronaphtha-lene was obtained from *m*-nitrobenzaldehyde (1·2 g.), ketone (1·5 g.), potassium hydroxide (0·5 g. in 2 c.c. of water) and alcohol (30 c.c.). The solution on adding potassium hydroxide turned dark in colour and at once solidified. The condensate was filtered at the pump and washed with a little alcohol, m.p. 175°. On recrystallisation from alcohol-chloroform it was obtained in light yellow shining plates, m.p. 190°, soluble in ethanol, methanol, acetone, and insoluble in ether and petroleum ether. (Found in material dried at 100° in *vacuo*: C, 67·21; H, 5·23 ; N, 4·36. $C_{19}H_{17}O_5N$ requires C, 67·25; H, 5·01 ; N, 4·12 per cent). Likewise derivatives with *o*- and *p*-nitro-benzaldehydes were prepared but they are dark brown amorphous powder and melted at 152° and 270° respectively and are soluble in chloroform, acetone and ethyl acetate. (Found in *p*-nitrobenzylidene derivative after

drying at 100° in *vacuo* : N, 4·13. $C_{19}H_{17}O_5N$ requires N, 4·12 per cent).

Condensation of the Ketone with Acetaldehyde, Formaldehyde and Crotonaldehyde.—Acetaldehyde (0·56 g.), alcohol (20 c.c) and ketone (1·5 g.) were refluxed in the presence of potassium hydroxide (0·5 g) and on working up a thick oily substance was obtained. Likewise similar products were obtained with formaldehyde and crotonaldehyde.

Oxidation of 1-Keto-2-benzylidene-6:7-dimethoxy-1:2:3:4-tetrahydro-naphthalene with Potassium Permanganate.—To a solution of the ketone (4·26 g.) in acetone at 0° finely powdered potassium permanganate (6 g.) was gradually added with constant stirring. The pink solution was filtered at the pump from the slimy precipitate and after destroying excess of potassium permanganate with alcohol it gave some unreacted ketone. The slimy precipitate was dissolved in water and its ether extract after acidification with dilute hydrochloric acid gave a mixture of benzoic acid and an acid with a brownish tinge, m.p. 174-78°. The latter was not sufficient for further characterisation and confirmation. During the course of work some sticky products were also obtained from which nothing definite could be isolated.

The micro-analyses were done by Dr. Ing. A. Schöller, Berlin. The authors express their thanks to Capt. M. Haidar, Chairman of the Chemistry Department for the facilities offered during this investigation.

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STRYCHNINE AND BRUCINE. PART IV. • A NOTE ON *ISO*STRYCHNIC ACID.

By RAFAT HUSAIN SIDDIQUI.

*iso*Strychnic acid is monobasic, gives crystalline salts and undergoes cyclisation with benzoyl chloride and acetic anhydride and with the latter gives *O*-acetyl derivative With 50% nitric acid it gives dinitro-*iso*strychnic acid and an amorphous acid.

Perkin and Robinson (*J. Chem. Soc.*, 1927, 2396) reported that *iso*-strychnic acid could neither be benzoylated nor reduced with hydrogen and palladium, while Ciusa described a benzoyl derivative (*Gazzetta*, 1928, **58**, 774). The acid after purification and crystallisation (*vide* experimental) had m.p. 240° and on treatment with acetic anhydride gave *O* acetyl*iso*strychnine, m.p. 195-96° (m p. 133-34° ; *O*-acetyldihydro-strychnine, m.p. 195-96°, *J. Chem. Soc.*, 1927, 2389 ; Cisua, *Atti. R. Acad. Lincci*, 1919, **28**, 185) while after treatment with benzoyl chloride only *iso*strychnine could be isolated The acid could not be nitrated with 5% and 10% hot nitric acid but 20% nitric acid gave an amorphous powder (Tafel, *Annalen*, 1898, **301**, 285) and with 50% nitric acid crystalline dinitro*iso*strychnic acid nitrate and a second amorphous acid, agreeing with the formula $C_{21}H_{24}O_9N_4$, $3\frac{1}{2}H_2O$, was isolated. *iso*Strychnic acid as well as its acetyl and dinitro derivatives give crystalline salts.

*iso*Strychnic acid as well as *iso*strychnine was accommodated in the formulae of strychnine by Perkin, Robinson and others (*J. Chem. Soc.*, 1910, 3051 ; *Gazzetta*, 1924, **54**, 516). The modifications of the strychnine formula have to take cognisance of this substance. The acid, like strychnic acid, is an iminocarboxylic acid and behaves as a monoacid base. Perkin and Robinson pointed out that the acid contains a molecule of water which is probably constitutionally bound, but it is shown in this paper that it is water of crystallisation as half of it is lost at 135° in *vacuo*. Strychnine and its derivatives are known to part with solvent of crystallisation with great difficulty. The acid shows the presence of a hydroxyl group in the molecule as evidenced by its acetylation and its cyclisation to *iso*strychnine with acetic anhydride. The alcoholic hydroxyl is postulated to be formed by scission of the oxide ring of strychnine and the carboxyl group by the rupture of the cyclic amide group under the influence of basic catalysts such as barium hydroxide and sodium ethoxide. The reaction is not fully understood

but it is certain that the ether oxygen atom and the N·CO·CH₂- group are involved. The formation of an acetyl derivative, the existence of a carboxyl group together with the fact that *iso*strychnine and its derivatives do not give *iso*nitroso or benzylidene derivatives support the view. *iso*-Strychnine has a double bond and on reduction gives dihydro*iso*strychnine, distinct from dihydrostrychnine, and thus the isomerism of the two is independent of double bond. Besides these some other changes also take place in the molecule. Pictet and Bacovescu have shown that a sulphonic acid of *iso*strychnine could not be isolated and that the molecule is readily oxidised by potassium permanganate. Similar discrepancy is observed in the present investigation as dinitro*iso*strychnic acid can not be reduced, while the corresponding dinitrostrychnic acid under identical conditions gives diaminostrychnine.

It is probable that under the influence of basic catalysts a number of deep-seated changes takes place in the strychnine molecule and an extensive study of the subject is necessary to solve the problem.

E X P E R I M E N T A L.

iso*Strychnic Acid, its Salts and Derivatives*.

iso*Strychnic acid* was prepared by heating strychnine with barium hydroxide and water in an autoclave and was isolated in clusters of prisms. The impure crystalline acid was dissolved in the least quantity of dilute sodium hydroxide solution, and after adding sufficient alcohol and ether to keep the whole into solution, the dark impurities which separated were removed. From the light orange solution, amorphous cream-coloured *iso*strychnic acid was precipitated with acetic acid, well washed with water and alcohol and then crystallised from methyl alcoholic acetic acid in snow-white small prisms, m.p 240° (decomp.) (Perkin and Robinson, *J. Chem Soc.*, 1927, 2396, give m.p. 231°). Its solution in concentrated sulphuric acid with a little potassium dichromate gave greenish yellow colour which finally turned green but with 60% sulphuric acid an orange-red solution was obtained ; with a crystal of potassium chlorate in concentrated sulphuric acid it turned red and in concentrated and dilute hydrochloric acid with a little potassium dichromate, a red solution was obtained which soon turned into deep blood or cherry colour. It crystallised with one mol. of water, half of which was lost at 135°. (Found : loss, 1·8. ½H₂O requires 2·5 per cent). (Found in material dried at 135° in *vacuo* : C, 70·0 ; H, 7·6 ; N, 8·1. C₂₁H₂₄O₃N₂, ½H₂O requires C, 69·8 ; H, 7·8 ; N, 7·8 per cent).

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The *hydrochloride*, precipitated by adding ether to a clear solution of the acid in a few drops of methyl alcoholic hydrochloric acid, was crystallised from alcohol-ether mixture in needles, m.p. 190-95° (frothing). (Found in material dried at 110°: Cl, 8·5. $C_{21}H_{24}O_3N_2$, H_2O, HCl requires Cl, 8·7 per cent).

The *picrate* was prepared in acetone solution. The residue after removal of acetone was well washed with acetone-ether mixture and crystallised from methyl alcohol in pale yellow prisms, m.p. 187-89° (decomp. 130°).

Action of Acetic Anhydride on isoStrychnic Acid : *Acetylisostrychnine.* —isoStrychnic acid (2 g.) was heated with acetic anhydride (5 c.c.) at 100° for 5 minutes, when the acid dissolved to a red solution which after dilution with water (50 c.c.) was further heated for $\frac{1}{2}$ hour. The filtered solution after cooling was made alkaline with ammonia and was extracted with chloroform. The residue from the dry chloroform extract was crystallised from alcohol-chloroform in prisms, m.p. 195-96° (decomp.). The substance is sparingly soluble in alcohol. A solution of the base in concentrated sulphuric acid with a little potassium dichromate turned light violet and finally on long keeping brown, but if the solution was diluted with water the violet colour turned into golden yellow. The sulphuric acid solution of the base with a trace of potassium chlorate turned light greenish yellow which on dilution and keeping developed a light pink tinge, while the base in concentrated hydrochloric acid produced a golden yellow colour. At 100° in *vacuo* it lost 2 mols. H_2O (Found in material dried at 100° in *vacuo*: C, 69·3 ; H, 6·9 ; N, 6·9 ; $COCH_3$, 9·8. $C_{21}H_{22}O_2N_2$ $COCH_3$, H_2O requires C, 69·8 ; H, 6·8 ; N, 7·1 , $COCH_3$, 10·9 per cent).

The *hydrochloride* was obtained as a microcrystalline powder by adding dry hydrogen chloride in ether to a chloroform solution of the base. After reprecipitation with ether from methyl alcoholic solution it had m.p. 225-26°. (Found in material dried at 100° in *vacuo* : Cl, 8·2. $C_{23}H_{27}O_4N_2$, HCl requires Cl, 8·2 per cent).

The *picrate* was obtained by adding ether solution of picric acid to a chloroform solution of the base and is soluble in alcohol and water, m.p. 184° (decomp.).

Action of Benzoyl Chloride on isoStrychnic Acid: *Formation of* iso-Strychnine.—isoStrychnic acid (2 g.) was suspended in dry pyridine and benzoyl chloride (0·9 g.) was added in the ice-cold ; the substance dissolved on shaking and the resultant red solution on standing overnight deposited a crystalline hydrochloride, which was well washed with ether and dried in *vacuo* over phosphorus pentoxide. The ether solution furnished benzoic

acid. The hydrochloride was recrystallised from methyl alcohol but only
1·2 g. could be obtained and no definite product could be isolated from
the mother-liquors. The crystalline hydrochloride was dissolved in chloro-
form, made alkaline with a drop of alcoholic potassium hydroxide and the
solution dried over sodium sulphate. The straw-coloured solution on
keeping deposited prisms which after washing with a little water and
alcohol had m.p. 219-20° (decomp.). It gave the same colour reactions as
*iso*strychnic acid. (Found in material dried at 100° in *vacuo* : C, 68·0 ;
H, 7·2 ; N, 7·4. $C_{21}H_{22}O_2N_2$, $2H_2O$ requires C, 68·10 ; H, 7·00 ; N, 7 57
per cent). Obviously it was *iso*strychnine (*cf. J. Chem Soc.*, 1927, 2389,
where m.p. 220° is recorded).

Action of Nitric Acid on iso*Strychnic Acid.*—Nitration was tried with
5% and 10% nitric acid by refluxing the acid for several hours but no
definite substance could be isolated. Nitric acid (20%) gave an amorphous
dinitro*iso*-acid (*cf.* Tafel, *loc. cit.*), but on raising the concentration to 50%
well defined products were obtained. *iso*Strychnic acid (5 g.) was dissolved
in 50% nitric acid in a glass dish and heated on the boiling water-bath with
constant stirring when the solution turned deep red and finally faded to a
deep orange-yellow colour with simultaneous evolution of nitrous fumes and
separation of a dull yellow crystalline powder in prisms. (A, 3 g.). The
whole process took about 5-7 minutes. The filtrate on dilution with water
gave an amorphous brown-red precipitate (B, 0·8 g.).

Fraction B.—The amorphous acid charred from 260-70° and was solu-
ble in methanol, dissolved sparingly in ethanol and readily in acetone. It
was also soluble in ammonia, alkalis and in acetic acid from which it came
down on dilution with water. The acid could not be induced to crystallise
and gave the following analytical data after drying at 100° in *vacuo*. (Found :
C, 46·8 ; H, 6·0 ; N, 10·1 per cent).

Fraction A : Dinitroisostrychnic Acid.—This mass was obtained in aggre-
gates of prisms when the hydrochloric acid solution of " A " was filtered
into dilute ammonia containing a little alcohol. It was washed with water
and alcohol. It is insoluble in alcohol, water and other common organic
solvents and it does not melt below 325°. (Found in material dried at 100°
in *vacuo* : C, 53·43 ; H, 5·3 ; N, 11·6. $C_{21}H_{22}O_7N_4$, $1\frac{1}{2}H_2O$ requires
C, 53·7 ; H, 5·3 ; N, 12·0 per cent). The acid like dinitrostrychnic acid
is basic in character and forms well defined crystalline salts which do
not melt below 325°.

The *hydrochloride*, sparingly soluble in alcohol, was obtained in
aggregates of needles when the acid was dissolved in dilute hydrochloric
acid or methyl alcoholic hydrochloric acid.

The *sulphate* was obtained in long needles on addition of methyl alcohol to a sulphuric acid solution of dinitro*iso*strychnic acid nitrate. .

Action of Reducing Agents on Dinitroisostrychnic Acid.—Dinitro*iso*strychnic acid (1·8 g.), concentrated hydrochloric acid (5 c.c.), and zinc (2 g.) were warmed on the boiling water-bath when the deep red solution turned greenish, bluish and finally slightly red in colour. The filtered solution on cooling was made ammoniacal with concentrated ammonia, zinc removed with hydrogen sulphide but nothing definite could be isolated from the dark filtrate.

Stannous chloride and hydrochloric acid and methyl alcoholic hydrochloric acid and iron did not give any definite reduction products.

EXPERIMENTS ON THE SYNTHESIS OF KETO-ACIDS. SYNTHESIS OF 2-*P*-METHOXYPHENYLCYCLO-PENTANONE-3-CARBOXYLIC ACID.

By Nripendra Nath Chatterjee and Girindra Nath Barpujari.

2-(*p*-Methoxyphenyl)-*cyclo*pentanone-3-carboxylic acid has been synthesised with a view to study a scheme of work for the synthesis of phenanthrene derivatives related to natural products.

Anisaldehyde cyanohydrin (I) is allowed to react with the sodium salt of ethyl cyanoacetate when the sodium derivative of ethyl $\alpha\beta$-dicyano-β-(*p*-methoxyphenyl)-propionate (II) is obtained. It is allowed to react with ethyl β-chloropropionate when diethyl $\alpha\beta$-dicyano-α-(*p*-methoxyphenyl)-*n*-butane-$\beta\delta$-dicarboxylate (III) is obtained. When hydrolysed by means of sulphuric acid (20%) the latter yields α-(*p*-methoxyphenyl)-*n*-butane-$\alpha\beta\delta$-tricarboxylic acid (IV), the triethyl ester of which undergoes cyclisation in presence of sodium in dry benzene to yield diethyl 2-(*p*-methoxyphenyl)-*cyclo*pentanone-3:5-dicarboxylate (V, $R=R'=CO_2Et$). This ester on hydrolysis and decarboxylation yields 2-(*p*-methoxyphenyl)-*cyclo*pentanone-3-carboxylic acid (V, $R=CO_2H$; $R'=H$).

(I)   (II)   (III)

(IV)   (V)

EXPERIMENTAL.

Anisaldehyde Cyanohydrin (I).—Anisaldehyde (60 g.) was added gradually to 200 c.c. of a solution of sodium bisulphite (250 g. of sodium bisulphite in 300 c.c. of water). The flask was shaken and cooled in ice during addition. The bisulphite compound was collected, washed with spirit (100 c.c.) and added gradually with stirring and cooling to a solution of potassium cyanide (60 g. of potassium cyanide in 90 c.c. of water). The heavy oil was then extracted with ether and washed successively with water, sodium bisulphite solution, water, sodium bicarbonate solution and finally with water. The ether solution was then dried over anhydrous sodium sulphate and the solvent removed under reduced pressure at 30° with the addition of two drops of concentrated sulphuric acid. The resultant oil solidified on standing in the refrigerator and the solid was then ground with petroleum ether (b.p. 30-60°), filtered off, washed with petroleum ether and recrystallised from ether-petroleum ether mixture, m.p. 67°, yield 60-70%.

Diethyl αβ-dicyano-α-(p-methoxyphenyl)-n-butane-βδ-dicarboxylate (III). —Ethyl cyanoacetate (96 g.) was added to an ice-cold solution of sodium (20 g.) in alcohol (240 c.c.) and anisaldehyde cyanohydrin (110 g.) was gradually added to the suspension of ethyl sodiocyanoacetate. Considerable heat was generated after each addition and it was found necessary to regulate the temperature by cooling in ice-water, and the clear red liquid was allowed to stand for 12 hours when the whole mass solidified to a red cake. The product of reaction was mixed with ethyl β-chloropropionate (106 g.) and after the initial reaction had abated was boiled under reflux for 15 hours. It was filtered and washed with dry ether. The filtrate was diluted with water and extracted with ether. The ethereal solution was washed with water, dried with calcium chloride and the solvent removed. The dicyano ester was distilled as a viscous liquid at 233-36°/4 mm., yield 45 g. (Found : C, 64·0 ; H, 6·3. $C_{19}H_{22}O_5N_2$ requires C, 63·6 ; H, 6·1 per cent).

α-(p-Methoxyphenyl)-n-butane-αβδ-tricarboxylic Acid (IV).—A solution of the above cyano-ester (III, 40 g.) in concentrated sulphuric acid (45 c.c.) was diluted with water (320 c.c.) and refluxed for 50 hours on a sand-bath. After cooling, the mixture was diluted with water and extracted with ether and the ethereal extract was treated with sodium carbonate solution. On acidification of the carbonate solution, the acid was obtained in the form of a gum which was extracted with ether. After drying over anhydrous sodium sulphate, the ether was removed and the gummy acid was kept in a vacuum desiccator, when it solidified. It was crystallised

from hot water, m.p. 183° (rapid heating), yield 20 g. (Found: C, 57·1; H, 5·4; Equiv., 101. $C_{14}H_{16}O_7$ requires C, 56·7; H, 5·4 per cent. Equiv. 98·67).

The *triethyl ester* was obtained in an almost quantitative yield from the acid by the alcohol vapour method. [The acid (30 g.), absolute alcohol (100 c.c.), concentrated sulphuric acid (9 c.c.), 4 litres of vapourised alcohol (4-5 hours)]. After dilution with a large volume of water, the ester was extracted with ether, the ethereal extract shaken with sodium bicarbonate solution and washed again, dried with sodium sulphate and ether removed. It was distilled at 205-15°/3 mm., yield 28 g. (Found: C, 63·4; H, 6·c. $C_{20}H_{28}O_7$ requires C, 63·1; H, 7·3 per cent).

Diethyl 2-*(p-Methoxyphenyl)-cyclopentanone-3 : 5-dicarboxylate* (V, R = R' = CO_2Et).—A mixture of the foregoing ester (30 g.) and molecular sodium (3·6 g.) in dry benzene (75 c.c.) was refluxed for 10 minutes to start the reaction. The heating was discontinued until the vigour of the reaction abated and heating was then continued for 2 hours. After cooling, the product was treated with cold dilute sulphuric acid and the benzene layer washed with aqueous sodium bicarbonate and with water, dried and solvent removed. The residue in alcoholic solution gave a reddish violet colouration with ferric chloride. The ester distilled with much decomposition at 202-212°/4 mm., yield 6 g. (Found: C, 65·1; H, 6·3. $C_{18}H_{22}O_6$ requires C, 64·6; H, 6·5 per cent).

2-*(p-Methoxyphenyl)-cyclopentanone-3-carboxylic Acid* (V, R = CO_2H; R' = H).—The above ester (10 g.) was refluxed with excess of dilute sulphuric acid (20%) for 14 hours and the cooled solution saturated with ammonium sulphate, repeatedly extracted with ether and the extract washed with water and dried. After removing ether it was kept in a desiccator when it crystallised. Recrystallised from ether it melted at 135°, yield 3 g. (Found: C, 66·7; H, 5·77. $C_{13}H_{14}O_4$ requires C, 66·67, H, 5·9 per cent).

The *semicarbazone* of the above keto-acid was crystallised from alcohol, m.p. 233°, (decomp.). (Found: N, 14·4. $C_{14}H_{17}O_4N_3$ requires N, 14·4 per cent).

Ethyl αβ-Dicyano-β-(p-methoxyphenyl)-propionate (II).—Anisaldehyde cyanohydrin (55 g.) was condensed with ethyl sodiocyanoacetate, prepared from ethyl cyanoacetate (48 g.) as before. The product was then poured into water and the solution acidified with hydrochloric acid. The separating o.l was extracted with ether, the ethereal extract washed several times with water, then thoroughly with a dilute solution of sodium carbonate and after drying over calcium chloride evaporated. The dicyano-ester was distilled

as a viscous liquid at 225°/5 mm., which solidifies in a vacuum desiccator over sulphuric acid. It was crystallised from alcohol as colourless crystals, m.p. 81°, yield 30 g. (Found : N, 11·1. $C_{14}H_{14}O_3N_2$ requires N, 10·85 per cent).

The sodium carbonate washing from the ethereal solution gave an acid containing nitrogen and crystallised from alcohol in needle-shaped crystals, m.p. 226°. Since the quantity formed was too small an investigation of its constitution could not be made.

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EXPERIMENTS ON THE SYNTHESIS OF KETO-ACIDS. ACTION OF SODIUM ETHOXIDE ON DIETHYL CYCLOPENTANONE-2-CARBOXYLATE-2-ACETATE.

By Nripendra Nath Chatterjee, Basanta Kumar Das
and Girindra Nath Barpujari.

Diethyl *cyclo*pentanone-2-carboxylate-2-acetate yields ethyl 5-carbethoxy*cyclo*pentanone-2-acetate by the action of sodium ethoxide in alcoholic solution.

During an investigation on the synthesis of carvestrene it was observed by Perkin and co-workers (*J. Chem. Soc.*, 1909, **95**, 2010) that ethyl pentane-αδε-tricarboxylate (I) is cyclised in presence of sodium in benzene to ethyl *cyclo*hexanone-3 : 6-dicarboxylate (II), although there is the possibility of the formation of the other isomer namely, ethyl 5-carbethoxy-*cyclo*pentanone-2-acetate (III, R=H).

In course of a synthetic work it is observed that diethyl *cyclo*pentanone-2-carboxylate-2-acetate, obtained from ethyl *cyclo*pentanone-2-carboxylate and ethyl chloroacetate, is transformed by boiling sodium ethoxide into 5-carbethoxy*cyclo*pentanone-2-acetate (III, R=H), the mechanism being obviously alcoholysis to ester (I) and subsequent ring-closure in a new position. It is our experience, however, that the five carbon ring is almost invariably formed in preference to the six carbon ring, where the two possibilities simultaneously exist. The constitution of the ester (III) is established by hydrolysis to *cyclo*pentanone-2-acetic acid (IV, R=H). As it is quite possible that *cyclo*pentanone-2-acetic acid may be obtained from the unchanged ethyl *cyclo*pentanone-2-carboxylate-2-acetate, an additional rigid proof of the constitution of the ester is afforded herein. Diethyl 5-carbethoxy*cyclo*pentanone-2-acetate-5-propionate (VI), obtained by the action of ethyl β-chloropropionate on the sodium salt of (III, R=H), on hydrolysis yields an acid which is identical in all respects with *cyclo*pentanone-2-acetic-5-propionic acid (VIII), prepared by a rational synthesis.

Ethyl *cyclo*pentanone-2-carboxylate-2-propionate, obtained by the action of ethyl β-chloropropionate on the sodium salt of ethyl *cyclo*pentanone-2-carboxylate, is transformed by boiling sodium ethoxide into ethyl 5-carbethoxy*cyclo*pentanone-2-propionate (V, R=H). The possibility of the formation of a six carbon ring does not exist in this case. Diethyl 5-carbethoxy*cyclo*pentanone-2-propionate-5-acetate (VII), obtained by the action

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of ethyl chloroacetate on (V, R=H) yields the required *cyclo*pentanone-2-acetic-5-propionic acid (VIII, R=CH₂) on hydrolysis.

That the transformation product is not a mixture of the esters (II) and (III, R=H) is evident from the observation that ethyl *cyclo*pentanone-2-acetate, obtained as a product of hydrolysis and esterification of the transformation product, yields an almost quantitative yield of a semicarbazone having melting point and mixed melting point 174° (*cf.* Linstead and Meade, *J. Chem. Soc.*, 1934, 935).

Diethyl 5-carbethoxy*cyclo*pentanone-2:5-diacetate (III, R=CH₂·CO₂·Et) and diethyl 5-carbethoxy-*cyclo*pentanone-2:5-dipropionate (V, R=CH₂·CH₂·CO₂Et, obtained by introducing an acetic acid and propionic acid residue in esters (III, R=H) and (V, R=H) respectively, yield *cyclo*pentanone-2 : 5-diacetic acid and *cyclo*pentanone-2 : 5-dipropionic acid on hydrolysis.

<div align="center">E X P E R I M E N T A L.</div>

*Ethyl 5-Carbethoxy*cyclo*pentanone-2-acetate* (III, R=H).—Diethyl cyclopentanone-2-carboxylate-2-acetate, required for the preparation of the above compound, was prepared as follows :—Finely divided metallic sodium (7·4 g.) in dry benzene (267 c.c.) was slowly treated with ethyl cyclopentanone-2-carboxylate (50 g.). The mixture was then refluxed on the water-bath for 2 hours. It was allowed to cool and ethyl chloroacetate (44 g.) added and further refluxed for 4 hours. It was then cooled, diluted with water and extracted with ether. The ether-benzene layer was washed with water, dried over calcium chloride, the solvents removed and the residual oil was distilled at 142-44°/4 mm. A mixture of diethyl cyclopentanone-2-carboxylate-2-acetate (80 g.) and alcoholic sodium ethoxide (8·3 g. sodium and 138 c.c. of alcohol) was refluxed for 8 hours on the sand-bath. The product was treated with ice-cold dilute sulphuric acid and extracted with ether, the ethereal extract was washed with water, dried over sodium sulphate and the ether removed. It was then distilled at 160-65°/6 mm., yield 60 g. It gives deep violet colouration with ferric chloride (*cf.* Perkin and co-workers, *loc. cit.*). (Found : C, 59·87; H, 7·5. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·4 per cent).

cyclo*Pentanone-2-acetic Acid* (IV, R=H).—The above ester was hydrolysed with two volumes of boiling concentrated hydrochloric acid. Hydrolysis was completed in 1 hour and 5 hours more were required for decarboxylation. After removal of the mineral acid under reduced pressure, cyclopentanone-2-acetic acid was distilled at 170-80°/5 mm. as an oil which soon solidified, m.p. 51-53° (mixed m.p.) (Linstead and Meade, *loc. cit.*).

The *semicarbazone* of the above keto-acid crystallised from alcohol, m.p. 198°. (Found : N, 21·0. $C_8H_{13}O_3N_3$ requires N, 21·1 per cent). cyclo*Pentanone-2-acetic acid was also obtained by the method of Linstead and Meade (*loc. cit.*) in order to compare the m.p. of its semicarbazone with that of the above keto-acid. In a typical experiment 5 g. of ethyl cyclopentanone-2-carboxylate-2-acetate was hydrolysed with two volumes of boiling concentrated hydrochloric acid. After removal of the mineral acid under reduced pressure, cyclopentanone-2-acetic acid was distilled at 170-80°/5 mm., as an oil which soon solidified. It was converted into semicarbazone in the usual manner. The semicarbazone melted at 198° in agreement with that of the above keto-acid (mixed m.p.).

Semicarbazone of Ethyl cyclo*Pentanone-2-acetate.*—cyclo*Pentanone-2-acetic acid, obtained as described above, was esterified by keeping overnight at room temperature with 3 parts of alcohol saturated with hydrogen chloride.

It was obtained in 90% yield, b.p. 123°/13 mm. The semicarbazone, obtained in an almost quantitative yield, melted at 174° (cf. Linstead and Meade, loc. cit.).

*Diethyl 5-Carbethoxy*cyclo*pentanone-2 : 5-diacetate* (III, R=CO_2Et).— Ethyl 5-carbethoxy*cyclo*pentanone-2-acetate (60 g.) was heated with a suspension of molecular sodium (6·5 g.) in benzene (120 c.c.) for 2 hours. The orange liquid was cooled and ethyl chloroacetate (40 c.c.) introduced and the mixture refluxed for 5 hours. The reaction product was mixed with water and a few drops of hydrochloric acid and the ester was isolated by means of ether, ether washed, dried and the ether removed. It was then distilled at 190-200°/8 mm., yield 30 g. (Found : C, 58·3; H, 7·2. $C_{16}H_{24}O_7$ requires C, 58·5; H, 7·3 per cent).

cyclo*Pentanone-2 : 5-diacetic Acid.*— A mixture of the above ester (30 g.) and concentrated hydrochloric acid (240 c.c.) was refluxed for 1 hour and the clear solution evaporated to dryness, finally under reduced pressure. The residual crystalline solid was washed with saturated aqueous ammonium sulphate and then with a little water, dried at 100°, and crystallised from a mixture of ethyl acetate and petroleum, m.p. 177°, yield 18 g. (Found : C, 53·9 ; H, 5·94. $C_9H_{12}O_5$ requires C, 54·0; H, 6·0 per cent).

The *diethyl* ester was prepared by esterification of the above acid (10 g.) by means of alcohol (50 c.c) saturated with hydrogen chloride at 0°. It was kept overnight and then refluxed for 7 hours. After dilution it was extracted with ether, the ethereal extract washed with sodium carbonate solution, then with water. After removal of ether, it was distilled at 168-170°/6 mm, yield 8 g. (Found: C, 60·8 ; H, 7·75. $C_{13}H_{20}O_5$ requires C, 60·9 ; H, 7·8 per cent).

*Ethyl 5-Carbethoxy*cyclo*pentanone-2-acetate-5-propionate* (VI).—Ethyl 5-carbethoxy*cyclo*pentanone-2-acetate (15 g.) was heated with a suspension of molecular sodium (1·6 g.) in benzene (30 c.c.) for 2 hours. The orange liquid was cooled and ethyl β-chloropropionate (10 c.c.) introduced and the mixture was refluxed for 5 hours. The reaction product was mixed with water and a few drops of hydrochloric acid and the ester was isolated by means of ether, ether washed, dried and the ether removed. It was then distilled at 200°/4 mm., yield 10 g. (Found : C, 59·7 ; H, 7·4. $C_{17}H_{26}O_7$ requires C, 59·65 ; H, 7·6 per cent).

cyclo*Pentanone-2-acetic-5-propionic Acid* (VIII).—A mixture of the above ester (10 g.) and concentrated hydrochloric acid (80 c.c.) was refluxed for 1 hour and the clear solution was then evaporated to dryness under reduced pressure. The residue crystallised and the solid was collected, washed with saturated aqueous ammonium sulphate and then with a little

water, dried at 100°, and recrystallised from a mixture of ethyl acetate and petroleum, m.p. 126°, yield 5 g. (Found : C, 56·6; H, 6·4. $C_{10}H_{14}O_5$ requires C, 56·1 ; H, 6·5 per cent).

The *diethyl ester* was prepared by esterifying the above acid (5 g.) by means of alcohol (25 c.c.), saturated with hydrogen chloride at 0°. It was kept overnight and then refluxed for 7 hours. After dilution it was extracted with ether, the ethereal extract washed with sodium carbonate solution, and then with water. After removal of ether, it was distilled at 170°/4 mm. (Found : C, 62·2; H, 8·1. $C_{14}H_{22}O_5$ requires C, 62·2 ; H, 8·1 per cent).

*Ethyl 5-Carbethoxy*cyclo*pentanone-2-propionate* (V, R = H).—Ethyl cyclopentanone-2-carboxylate-2-β-propionate was prepared in the following manner Ethyl cyclopentanone-2-carboxylate (52 g.) was added to molecular sodium (8 g.) in benzene (400 c.c.). After 1 hour the sodium compound was cooled and slowly treated with ethyl β-chloropropionate (41 g.). After heating for 5 hours more on the steam-bath, the mixture was acidified and the benzene layer was washed with sodium carbonate solution. Ethyl cyclopentanone-2-carboxylate-2-β-propionate (56 g., b. p. 189°/18 mm.) was obtained. A mixture of ethyl cyclopentanone-2 carboxylate-2-β-propionate (45 g.) and alcoholic sodium ethoxide (4·5 g. of sodium in 66 c.c. of alcohol) was refluxed for 8 hours on the sand-bath. The product was treated with ice-cold dilute sulphuric acid and extracted with ether and after removing ether it was distilled at 175°/4 mm. It gives deep violet colouration with alcoholic ferric chloride, yield 26 g. (Found : C, 60·9 ; H, 7·8. $C_{13}H_{20}O_5$ requires C, 60·9 ; H, 8·1 per cent).

*Ethyl 5-Carbethoxy*cyclo*pentanone-2-propionate-5-acetate* (VII). — Ethyl 5-carbethoxycyclopentanone-2-propionate (26 g.) was heated with a suspension of sodium powder (2·8 g.) in benzene (55 c.c.) for 2 hours. The orange liquid was cooled and ethyl chloroacetate (13 g.) introduced and the mixture refluxed for 5 hours. The reaction product was mixed with water and a few drops of hydrochloric acid and the ester was isolated by means of ether. The ethereal extract was washed with water, dried and the solvent removed. It was then distilled at 205°/4 mm., yield 15 g. (Found : C, 59·8 ; H, 7·4. $C_{17}H_{26}O_7$ requires C, 59·65 ; H, 7·6 per cent).

cyclo*Pentanone-2-acetic-5-propionic Acid* (VIII).—A mixture of ethyl 5-carbethoxycyclopentanone-2-propionate-5-acetate (15 g.) and concentrated hydrochloric acid (120 c.c.) was refluxed for 1 hour and the clear solution was then evaporated under reduced pressure. The residue crystallised and the solid was collected, washed with saturated aqueous ammonium sulphate

and then with little water, dried at 100°, and recrystallised from a mixture of ethyl acetate and petroleum, m.p. 126° (mixed m.p.), yield 6 g. (Found : C, 56·1 ; H, 6·6. $C_{10}H_{14}O_5$ requires C, 56·1 ; H, 6·5 per cent).

Ethyl 5-Carbethoxycyclopentanone-2 : 5-dipropionate (V, $R=CH_2 \cdot CH_2 \cdot CO_2Et$).—Ethyl 5-carbethoxy*cyclo*pentanone-2-propionate (48 g.) was heated with a suspension of sodium powder (5·2 g.) in benzene (100 c.c.) for 2 hours. The cold liquid was treated with ethyl β-chloropropionate (24 g) and the mixture refluxed for 5 hours. The reaction product was mixed with water and a few drops of hydrochloric acid and the ester was isolated with ether. The ethereal extract was washed with water, dried and the solvent removed. It was then distilled at 215°/4 mm. (Found : C, 60·9 ; H, 8 1. $C_{18}H_{28}O_7$ requires C, 60·7 ; H, 7·8 per cent).

cycloPentanone-2 : 5-dipropionic Acid.—A mixture of ethyl 5-carbethoxy-*cyclo*pentanone 2 : 5-dipropionate (25 g.) and concentrated hydrochloric acid (200 c.c.) was refluxed for 1 hour and the clear solution was then evaporated under reduced pressure. The solid obtained was collected, washed with saturated aqueous ammonium sulphate and then with a little water, dried at 100° and crystallised from a mixture of ethyl acetate and petroleum ether, m.p. 122°. (Found : C, 57·9 ; H, 6·8. $C_{11}H_{16}O_5$ requires C, 57·9 ; H, 6·8 per cent)

The *diethyl ester* was prepared by esterification of the above acid by means of alcohol saturated at 0° with hydrogen chloride. It was kept overnight and then refluxed for 7 hours. After dilution it was extracted with ether, the ethereal extract washed with sodium carbonate, water and dried. After removing ether, the ester was distilled at 172°/4 mm. (Found : C, 63·6 ; H, 8·4. $C_{15}H_{24}O_5$ requires C, 63·3 ; H, 8·4 per cent).

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THE ACTION OF CHLORINE ON THE HYDROXIDES OF LITHIUM AND POTASSIUM IN THE PRESENCE OF IODINE. PART I.

BY. R. K. BAHL, AND SURJIT SINGH.

By passing a brisk current of chlorine through a boiling solution of iodine in lithium hydroxide and potassium hydroxide, dihydrated lithium diparaperiodate, $Li_8I_2O_{11}$, $2H_2O$ or $4Li_2O$, I_2O_7, $2H_2O$ and potassium metaperiodate, KIO_4 were obtained respectively.

Ammermüller and Manus (*Ann. Physik*, 1833, **28**, 514) prepared di-sodium paraperiodate, $Na_2H_3IO_6$, by passing chlorine into a solution of equal parts of sodium hydroxide and iodate. Wells (*Amer. Chem. J.*, 1901, **26**, 278) prepared the same salt by passing a brisk current of chlorine into a boiling solution of sodium hydroxide in the presence of finely powdered iodine. This result was confirmed by Partington and Bahl (*J. Chem Soc.*, 1934, 1091). We have tried this method of obtaining a periodate in the case of lithium and potassium which have been found to yield dihydrated lithium diparaperiodate, $Li_8I_2O_{11}$, $2H_2O$ or $4Li_2O$, I_2O_7, $2H_2O$ and potassium metaperiodate, KIO_4 respectively.

Analyses of these salts with respect to the alkali metal as sulphate and iodine and available oxygen by the method of Partington and Bahl (*J. Chem. Soc.*, 1934, 1085, 1087), have been presented below.

Lithium Salt.

Sample.	Lithium	Iodine.	Available oxygen.
1	10·990%	48·525%	21·165%
2	10·619	48·244	21·379
3	11·00	48·767	21·015

These values show that the lithium salt obtained is a dihydrated lithium diparaperiodate, $Li_8I_2O_{11}$. $2H_2O$ or $4Li_2O$, I_2O_7, $2H_2O$. The calculated lithium and iodine values are 10·727 and 48·716% respectively. The available oxygen according to the decomposition

$$Li_8I_2O_{11}, 2H_2O = 4Li_2O + I_2 + 2H_2O + 3\tfrac{1}{2}O_2$$

is 21·455%.

Potassium Salt.

Sample A was prepared by passing chlorine through a boiling solution of iodine in potassium hydroxide.

Sample B was obtained on cooling the supernatant solution from the above.

Sample A.	K.	I.	Available oxygen.	Sample B.	K.	I.	Available oxygen.
1	16·735%	55·312%	28·030%	1	16·708%	55·267%	27·787%
2	17·141	55·513	28 236	2	17·043	55·398	27 857
3	16·637	55·212	27·787	3	16·759	55·273	27·500

These values agree with potassium metaperiodate, KIO_4, the calculated values of potassium and iodine being 16·957 and 55·217% respectively. The available oxygen according to the decomposition

$$2KIO_4 = K_2O + I_2 + 3\tfrac{1}{2}O_2$$

is 27·826%.

Ihre (*Ber.*, 1870, **3**, 316) also obtained the same salt by the oxidising action of chlorine on a hot solution containing potassium iodate and an excess of potassium hydroxide.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS. PART VIII. OXIDATION WITH CHLORAMINE-T.

By Balwant Singh and Ahsanulhaque Rehmann.

Hydroquinone, quinhydrone, hydrazine hydrochloride, potassium iodide, sodium bisulphite and sodium nitrite have been determined by titrating them potentiometrically at 15° against chloramine-T, using a platinum electrode coupled with a saturated calomel electrode.

Noll (*Chem. Ztg.*, 1924, **48**, 845) described the use of chloramine-T *i.e.*, the sodium compound of *p*-toluenesulphochloramide, as a reagent for oxidation purposes. The solid salt has the composition

$$p\text{-}CH_3\cdot C_6H_4\cdot SO_2\cdot N {\Large<}^{Na}_{Cl} \text{, } 3H_2O \text{ (M.W., 281·5).}$$

In solution it behaves like a stable hypochlorite

$$CH_3\cdot C_6H_4\cdot SO_2\cdot N {\Large<}^{Na}_{Cl} + H_2O = CH_3\cdot C_6H_4\cdot SO_2\cdot NH_2 + NaCl + O.$$

This reagent is finding increasing use in place of sodium hypochlorite. It has the advantage that its aqueous solution is stable in air and shows only slight deterioration over long periods when kept in a stoppered bottle; moreover, as alkali is absent, there is no risk of formation of chlorates, which lead to side-reactions.

This reacts in acid solution with potassium iodide to liberate iodine

$$CH_3\cdot C_6H_4\cdot SO_2\cdot N {\Large<}^{Na}_{Cl} + 2HI = CH_3\cdot C_6H_4\cdot SO_2\cdot NH_2 + NaCl + I_2$$

and this reaction is useful for its standardisation.

Rupp (*Pharm. Zentrl.*, 1925, **66**, 33) used chloramine-T for the determination of trivalent antimony, and later for the titration of stannous tin (*Z. anal. Chem.*, 1928, **73**, 51).

Tomicek and Sucharda (*Chem. Abs.*, 1932, **26**, 1210) used it as a reagent for the potentiometric determination of tervalent arsenic and antimony; bivalent tin and iron and the ferrocyanide and iodide ions; and for the visual titration of tervalent arsenic and antimony, using methyl red as indicator.

Komarovskii, Filonova and Korenman (*J. Appl. Chem. Russia*, 1933, **6**, 742 ; *Z. anal. Chem.*, 1934, **96**, 321) have shown that chloramine-T can be used as a volumetric reagent to replace the more expensive iodine and the

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·less stable hypochlorite in the estimation of ferrocyanide, hydrazine and hypophosphite.

In the volumetric estimations a crystal of potassium iodide and a few c.c. of starch solution are added and the solution titrated with chloramine-T. The presence of a slight excess of the reagent (end-point) is shown by the liberation of iodine and the appearance of the blue colour of starch iodide.

Chloramine-T oxidises hydroquinone, quinhydrone, hydrazine hydrochloride, potassium iodide, sodium bisulphite and sodium nitrite. The reactions are represented by the following equations :—

$$(1) \quad CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N{<}^{Na}_{Cl} + C_6H_4(OH)_2 = CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2 + NaCl + C_6H_4O_2$$

$$(2) \quad CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N{<}^{Na}_{Cl} + C_6H_4O_2 \cdot C_6H_4(OH)_2 = CH_3 C_6H_4 \cdot SO_2 \cdot NH_2 + NaCl + 2C_6H_4O_2$$

$$(3) \quad 2CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N{<}^{Na}_{Cl} + N_2H_4 = 2CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2 + 2NaCl + N_2$$

$$(4) \quad CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N{<}^{Na}_{Cl} + 2HI = CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2 + NaCl + I_2$$

$$(5) \quad CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N{<}^{Na}_{Cl} + NaHSO_3 + H_2O = CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2 + NaCl + NaHSO_4$$

$$(6) \quad CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N{<}^{Na}_{Cl} + HNO_2 = CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2 + NaCl + HNO_3$$

These reactions have been utilised in the quantitative determination of these substances by the potentiometric method.

EXPERIMENTAL.

The oxidation-reduction electrode, which consisted of a bright platinum foil immersed in the solution to be titrated, was coupled with a saturated calomel electrode. The cell was placed in a water-bath, the temperature of which was kept at 15°. The e.m.f. of the cell was read on a potentiometer.

A known weight of the substance was dissolved in water and acidified with hydrochloric acid except in case of nitrite. The solution was titrated potentiometrically against standard chloramine-T. The mixture was kept stirred very thoroughly with a mechanical stirrer.

In the case of sodium nitrite acetic acid was used. A known volume of a standard solution of chloramine-T was taken in the titration vessel, acidified with acetic acid and titrated against sodium nitrite solution.

The titrations of potassium iodide were conducted in an atmosphere of carbon dioxide.

The potentiometric readings were recorded after the addition of the reagent, when the potential acquired a steady value. A series of potentiometric titrations were performed with different amounts of each substance One titration as typical of the set is recorded in the following table.

TABLE I.

Titration of 0·1066 g. of hydroquinone mixed with water and acidified with dilute hydrochloric acid, against chloramine-T $(M/20)$.

Chloramine-T.	E.M.F.	E/C (m. volt/c.c.)	Chloramine-T.	E.M.F.	E/C (m. volt/c.c.)
0·00 c.c.	0·295 volts.		19·20 c.c	0·479 volts	
		43			460
2 00	0·381		19·25	0·502	
		3			1300
5·00	0·390		19·30	0·567	
		2			1760 (Maximum)
8·00	0·396		19·35	0·655	900
		2			
10·00	0·400		19·40	0·700	
		3			210
12·00	0·405		19·50	0·721	
		3			120
14 00	0·410		19·70	0·745	
		3			63
16·00	0·416		20·00	0·764	
		5			49
17·00	0 421		21·00	0·812	
		8			29
17·80	0·426		22·00	0·831	
		18			17
18·30	0·435		24·00	0·864	
		26			12
18·80	0·448		27·00	0·900	
		60			7
19·00	0·460		30·00	0·920	
		80			4
19·10	0·468		34·00	0·937	
		110			

DISCUSSION.

These titrations, except in the case of hydrazine hydrochloride, show that with the addition of the standard chloramine-T, the E.M.F. rose steadily till the equivalence-point. In the case of hydrazine hydrochloride, on first few additions of the titrant, the E.M.F. remained constant. This was followed by a steady rise till the equivalence-point on further addition of the reagent. At the equivalence-point there was a sharp jump in potential, followed by a steady rise in each case.

In the case of sodium nitrite, since it was used as the titrant, the
E.M.F. decreased steadily till the equivalence-point. At the equivalence-
point there was a sharp break in E.M.F. This was followed by a steady
decrease in potential.

From the volume of chloramine-T required in each case, corresponding
to the equivalence-point, the amount of the substance was calculated. In
the following table the values are compared with the amounts of the subs-
tance taken.

TABLE II.

Hydroquinone.		Quinhydrone.		Hydrazine hydrochloride.	
Taken.	Found.	Taken.	Found.	Taken.	Found.
0·1066 g.	0·1064 g.	0·1152 g.	0·1150 g.	0·0591 g.	0·0590 g.
0·1517	0·1513	0·2048	0·2045	0·0996	0·0990
0·2171	0·2168	0·2836	0·2835	0·1465	0·1462
0·2583	0·2580	0·3986	0·3981	0·1772	0·1768
0·3549	0·3543	0·4890	0·4884	0·2001	0·1995
				0·2416	0·2409

Sodium bisulphite.		Potassium iodide.		Sodium nitrite.	
0·0321 g.	0·0320 g.	0·0415 g.	0·0415 g.	0·0345 g.	0·0345 g.
0·0477	0·0477	0·0830	0·0830	0·0428	0·0428
0·0801	0·0800	0·1660	0·1660	0·0518	0·0518
0·1285	0·1283	0·2490	0·2490	0·0690	0·0690
0·1749	0·1746	0·3320	0·3320	0·1035	0·1035
				0·1380	0·1380

These results show that hydroquinone, quinhydrone, hydrazine hydro-
chloride, potassium iodide, sodium bisulphite and sodium nitrite can be
potentiometrically determined by using chloramine-T as the oxidising agent.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS. PART IX. OXIDATION WITH CHLOR-AMINE-T (INDIRECT QUANTITATIVE DETERMINATIONS).

BY BALWANT SINGH AND AHSANULHAQUE REHMANN.

Potassium iodate, potassium permanganate, potassium dichromate and potassium chromate have been determined indirectly by a potentiometric method. The excess of potassium iodide, added in each case, was titrated potentiometrically against chloramine-T at 15° in an atmosphere of carbon dioxide, using a platinum electrode coupled with a saturated calomel electrode.

In presence of sulphuric acid, potassium iodide reacts with chloramine-T, potassium iodate, potassium permanganate, potassium dichromate and potassium chromate with the following reactions :

(1) $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N \Big\langle {}^{Na}_{Cl} + H_2SO_4 + 2KI = CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2 + NaCl + K_2SO_4 + I_2$

(2) $KIO_3 + 3H_2SO_4 + 5KI = 3K_2SO_4 + 3H_2O + 3I_2$

(3) $2KMnO_4 + 8H_2SO_4 + 10KI = 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$

(4) $K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$

(5) $2K_2CrO_4 + 8H_2SO_4 + 6KI = 5K_2SO_4 + Cr_2(SO_4)_3 + 8H_2O + 3I_2$

These reactions have been made use of in the quantitative estimation of potassium iodate, potassium permanganate, potassium dichromate and potassium chromate.

EXPERIMENTAL.

A known weight of each substance was mixed with a known excess of potassium iodide, dissolved in water and the solution acidified with dilute sulphuric acid. The excess of potassium iodide was determined by titrating the mixture potentiometrically against standard chloramine-T. The titrations were conducted at 15°, in an atmosphere of carbon dioxide. The mixture was kept stirred with a mechanical stirrer.

A series of potentiometric titrations were performed with different amounts of each substance. One titration as typical of the set is recorded in the following table.

TABLE I.

Titration of 0·0342 g. of potassium iodate mixed with 0·2385 g. of potassium iodide, dissolved in water and acidified with dilute sulphuric acid, against chloramine-T ($N/20$).

Chloramine-T.	E.M.F.	E/C (m. volt./c.c.)	Chloramine-T.	E.M.F.	E/C (m. volt./c.c.)
0·00 c.c.	0·417 volts		12·45 c.c.	0·522 volts	
		1			180
2·00	0·420		12·50	0·531	
		4			220
5·00	0·432		12·60	0·542	
		5			240
7·00	0·441		12·65	0·554	
		6			520
9·00	0·453		12·70	0·580	
		7			2980 (Maximum)
10·00	0·460		12·75	0·729	
		14			500
11·00	0·474		12·80	0·754	
		20			280
11·50	0·484		12·90	0·782	
		23			100
11·80	0·491		13·00	0·792	
		25			55
12·00	0·496		13 40	0·814	
		40			42
12·20	0·504		14·00	0·839	
		50			9
12·30	0·509		15·00	0·848	
		60			8
12·35	0·512		17·00	0·863	
		80			7
12·40	0·516		20·00	0·884	
		120			4
			23·00	0·896	

DISCUSSION.

In these titrations, it is evident that with the addition of the titrant the E.M.F. rose steadily till the equivalence-point. At the equivalence-point there was a sharp jump in potential in each case followed by a steady rise in potential on further addition of the reagent.

From the volume of chloramine-T (C-T) used, corresponding to the equivalence-point in each titration, the amount of each substance was calculated. In the following table the values obtained are compared with the amounts of the substance taken.

TABLE II.

Potassium iodate

KIO₃ taken.	KI added.	Excess KI corersponding to C−T.	KI used for KIO₃.	KIO₃ found.
0·0342 g.	0·2385 g.	0·1058 g.	0·1327 g.	0·0342 g
0·0539	0·3447	0·1361	0·2086	0·0538
0·0856	0·4985	0·1671	0·3314	0·0854
0·1455	0·7412	0·1760	0·5652	0·1457
0·1883	1·0080	0·2780	0·7300	0·1883
0·2797	1·4430	0·3586	1·0844	0·2796

Potassium permanganate.

KMnO₄ taken.	KI added.	Excess KI corresponding to C−T.	KI used for KMnO₄.	KMnO₄ found.
0·0506 g.	0·3528 g.	0·0883 g.	0·2645 g.	0·0504 g.
0·0885	0·6041	0·1398	0·4643	0·0884
0·1264	0·8446	0·1813	0·6633	0·1263
0·1707	1·1264	0·2324	0·8940	0·1703
0·2086	1·3488	0·2548	1·0940	0·2084
0·2529	1·6768	0·3485	1·3283	0·2528

Potassium dichromate.

K₂Cr₂O₇ taken.	KI added.	Excess KI corresponding to C−T.	KI used for K₂Cr₂O₇.	K₂Cr₂O₇ found.
0·0490 g.	0·2589 g.	0·1033 g.	0·1656 g.	0·0489 g.
0·0883	0·4249	0·1261	0·2988	0·0883
0·1569	0·6754	0·1444	0·5310	0·1569
0·2062	0·8662	0·1603	0·6969	0·2059
0·2798	1·1618	0·2158	0·9460	0·2795
0·3534	1·4375	0·2432	1·1943	0·3528

TABLE II (*contd.*).

Potassium chromate.

K$_2$CrO$_4$ taken.	KI added.	Excess KI corresponding to C – T.	KI used for K$_2$CrO$_4$.	K$_2$Cr$_2$O$_4$ found.
0·0712 g.	0·3321 g.	0·1502 g.	0·1819 g.	0·0710 g.
0·1166	0·4300	0·1315	0·2985	0·1164
0·1683	0·6093	0·1779	0·4314	0·1683
0·2201	0·7636	0·1992	0·5644	0·2201
0·2839	0·9445	0·2158	0·7287	0·2842
0·3627	1·1067	0·1760	0·9307	0·3630

These results show that potassium iodate, potassium permanganate, potassium dichromate and potassium chromate can be indirectly determined by means of chloramine-T.

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DEPARTMENT OF CHEMISTRY,
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MAGNETIC STUDY OF THE POLYMERISATION OF STYRENE.

By S. S. Bhatnagar, P. L. Kapur and (Miss) Gurbaksh Kaur.

The magnetic study of the behaviour of styrene on polymerisation shows that the diamagnetic susceptibility goes on decreasing when the polymerisation occurs in vacuum, in presence of oxygen, on the other hand, the value falls slightly in the beginning and then rises, till after sixteen hours, it becomes greater than that of a sample polymerised in vacuum. The initial low value may be attributed to the intermediate formation of peroxides, usually of less diamagnetic character. The observed high susceptibility of polymerised styrene, which cannot be accounted for by Pascal's law, is regarded as the net result of the disappearance of double bonds in polymerisation and to its anisotropy.

Styrene polymerises to products of large molecular weights. The production of high polymers has been attributed by Whitby and Katz (*J. Amer. Chem. Soc.*, 1928, **50**, 1160) to the formation of a link between molecules by shifting a hydrogen atom along the chain. The formation of polystyrene according to this theory occurs as

$$\begin{array}{ccccccc}
C_6H_5 & & C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5 \\
| & \rightarrow & | & | \;\;\rightarrow & | & | & | \\
CH\!=\!CH_2 & & CH_2\!-\!CH_2\!-\!C\!=\!CH_2 & & CH_2\!-\!CH_2\!-\!CH\!-\!CH_2\!-\!C\!=\!CH_2
\end{array}$$

The theory implies that the formation of the highly polymeric products occurs in steps, each corresponding to a specific compound capable of isolation as such. Such processes lead only to the formation of relatively low molecular products and never to high polymers.

The formation of really high polymers has been explained by Staudinger (*Ber.*, 1931, **84**, 2093; *Trans. Faraday Soc.*, 1936, **32**, 104) by assuming that a molecule of the monomeric substance becomes activated and then reacts with a second molecule. The new molecule formed has active points on either of its ends and polymerises ; this process continues to form high polymers. He represents the structure of polystyrene as

$$\begin{array}{cccccc}
& C_6H_5 & C_6H_5 & C_6H_5 & & \\
& | & | & | & & \\
....C & -\; C & -\; C & -\; C & -\; C & -\; C.... \\
| & | & | & | & | & | \\
H & H_2 & H & H_2 & H & H_2
\end{array}$$

A long-chain polystyrene molecule is thus formed as a result of the disappearance of double bonds present in the original monomer.

In the present investigation the authors have undertaken to examine the process of polymerisation of styrene from the change in magnetic

5

properties which should take place if the disappearance of double bonds lead to polymerisation.

EXPERIMENTAL.

Pure colourless styrene was prepared from cinnamic acid (cf. Roger Adam, "Organic Synthesis", 1928, Vol. VIII, p. 84).

Styrene was sealed in a number of evacuated pyrex glass tubes which were heated in an electrically regulated thermostat kept at 98° ± 1°. After definite intervals of time a tube was taken out of the thermostat and cooled at room temperature, while the rest of the tubes were allowed to be heated further. The cooled tube was broken and the amount of polystyrene formed was determined by dissolving a known weight of the liquid in benzene, in which both the monomer and the polymer were soluble, and then precipitating the polymer from the solution by adding a large quantity of alcohol. After allowing to settle for some time it was filtered through a weighed sinter glass funnel, washed free from styrene with alcohol and dried in a steam oven.

The magnetic susceptibility of the cooled liquid was determined on a modified form of a Gouy's magnetic balance. Only the susceptibility of the liquids, heated for not more than 16 hours, could be determined, as those heated longer became too viscous to be transferred to the tube for measurements. It was found that reproducible result could be obtained only after great care. The mean values of several observations are tabulated below.

TABLE I.

Vacuum.

Time.	% Polystyrene.	Susceptibility × 10^7.	Time.	% Polystyrene	Susceptibility × 10^7.
Original	0	−6·575	8 hr.	17·5	−6·937
2 hr.	4	−6·713	10	22·5	−6·993
4	8·6	−6·811	12	27·5	−7·044
5	...	−6·857	15	...	−7·105
6	13·2	−6·878	16	39·3	−7·112

Oxygen.

Original	0	−6·575	6	16·0	−6·636
2 hr.	5·2	−6·560	8	21·2	−6·787
4	10·7	−6·553			

While repeating the above experiments a set of tubes was found to be not completely evacuated but contained some air. The results thus obtained are embodied in Table I.

From the results shown above it is clear that in vacuum the susceptibility value goes on increasing with increased polymerisation, whereas in the presence of air, although the percentage of polymerisation is more than that in vacuum, yet the susceptibility falls slightly at first and then begins to rise. Also it is observed that with the increase in the duration of heating the difference between the susceptibilities of the liquid heated in vacuum and that heated in air goes on diminishing. It is possible that after prolonged heating, the susceptibility of the liquid heated in air may be more than that of the one heated in vacuum, but this could not be verified for the reason mentioned above. Therefore, in order to compare the behaviour of the polymerisation of styrene in air and in vacuum under similar conditions, the following experiment was arranged : Two tubes with the same pull on Gouy's balance were made and an equal amount of styrene was put in both. One of them was sealed in the presence of air and the other was sealed after evacuation. Both the tubes were heated in a thermostat for equal intervals of time and cooled to the room temperature and the pull was determined on a Gouy's balance. The results are stated below.

TABLE II.

Time.	Deflection in mg. per g. of the specimen.		Time.	Deflection in mg. per g. of the specimen.	
	Vacuum.	Oxygen.		Vacuum.	Oxygen.
Original	124·5	124·0	10 hr.	137·5	133·0
2 hr.	126·5	123·5	12	140·0	138·0
4	129·5	123·0	16	143·5	144·0
6	132·5	125·5	20	145·5	148·0
8	134·5	128.0			

DISCUSSION.

Staudinger (loc. cit.) represents the structure of polystyrene as a long-chain of styrene groups formed by end to end combination at the olefine double bond as follows :—

$$\cdots \; \underset{\underset{H}{|}}{\overset{\overset{C_6H_5}{|}}{C}} - \underset{\underset{H_2}{|}}{C} - \underset{\underset{H}{|}}{\overset{\overset{C_6H_5}{|}}{C}} - \underset{\underset{H_2}{|}}{C} - \underset{\underset{H}{|}}{\overset{\overset{C_6H_5}{|}}{C}} - CH_2 \; \cdots$$

Much speculation, however, is rife as regards the indeterminateness of the formulae for polystyrene with free terminal valencies $-(CHPh-CH_2)_n-$. If the terminal valencies were free as suggested in the formula, the end carbons would behave like a free radical. From the magnetic standpoint the free radical should show strong paramagnetism and with the formation of a large number of polymers the diamagnetic susceptibility should fall, which is contrary to observation, because we find that with the increase in percentage of the polymers formed the diamagnetic susceptibiiity rises. It is therefore clear from the magnetic data that no free valency exists in the polymers.

Staudinger (*loc. cit.*) believes that as the process of polymerisation proceeds, an unknown side-reaction makes the free terminal valencies disappear. The first possibility is to suppose that ring formation occurs by the union of the two ends of the double chain.

$$
\begin{array}{ccccccc}
C_6H_5 & & C_6H_5 & & C_6H_5 & & \\
| & & | & & | & & \\
CH & -CH_2 & -C & -CH_2 & -C & -CH_2 \\
| & & | & & | & & | \\
& H & H & H & H & \\
| & & | & & | & & | \\
CH_2 & -C & -CH_2 & -C & -CH_2 & -CH \\
& | & & | & & | \\
& C_6H_5 & & C_6H_5 & & C_6H_5 \\
\end{array}
$$

Against this possibility there is not only the lack of experimental evidence, but the fact that since highly polymeric products are usually mixtures representing widely different degrees of polymerisation, it is necessary to believe that a large number of rings of different sizes are capable of formation with practically the same degree of ease. The second possibility is to suppose that the terminal valencies are satisfied by foreign elements or groups derived not from the parent substances but from the medium.

$$
\begin{array}{ccccccc}
C_6H_5 & & C_6H_5 & & C_6H_5 & & \\
| & & | & & | & & \\
A-C & -CH_2 & -C & -CH_2 & -C & -CH_2-B \\
| & & | & & | & & \\
H & & H & & H & & \\
\end{array}
$$

But the present investigation with pure styrene excludes such a possibility. Staudinger and Steinhöfer (*Annalen*, 1935, **517**, 35) consider it more likely that a polymer contains a double bond at one end, the mechanism of its formation involving the wandering of a hydrogen atom from the end of one chain to saturate the end of another. The existence of such a double

bond has recently been shown by Whitby (*Trans. Faraday Soc.*, 1936, **32**, 375) who found that polystyrene reacted with bromine. Moreover, he found that the amount of bromine that reacted with polystyrene corresponded to one double bond and the amount taken up was practically independent of the length of the polymer.

According to the last possibility, if n molecules of styrene, $Ph \cdot CH = CH_2$ polymerise, the polymer would contain one double bond and in the course of polymerisation $(n-1)$ double bonds would disappear.

From the magnetic standpoint the constitutive correction factor value λ for an allyl group double bond in styrene is $4 \cdot 51 \times 10^{-6}$. Therefore with the loss of one such bond the diamagnetic susceptibility of the product formed should rise by $4 \cdot 51 \times 10^{-6}$ units. When n molecules containing n allyl double bonds polymerise to form a polymer with only one such bond, the mass susceptibility of the polymer formed can be represented as

$$\chi = \frac{n\chi_s + (n-1)\lambda}{nM_s} \qquad \dots \text{ (1)}$$

where χ_s = molecular susceptibility of styrene, n = number of molecules of styrene which polymerise, λ = constitutive correction factor for an allyl group, M_s = mol. wt. of styrene.

If the whole of styrene were to polymerise to form polymers from 1000 molecules of styrene, the mass susceptibility of such a polymer according to equation (1) would be $-0 \cdot 701 \times 10^{-6}$, when the molecular susceptibility of styrene is taken to be $-68 \cdot 43 \times 10^{-6}$, and if $39 \cdot 3 \%$ were to polymerise the susceptibility value of the solution of polystyrene in styrene would be $-0 \cdot 675 \times 10^{-6}$. Actually, as is given in Table I, the value of χ for liquid containing $39 \cdot 3 \%$ of the polymer and the rest of the styrene is $-0 \cdot 711 \times 10^{-6}$. The observed value is much higher than the calculated one. It is, therefore, obvious that the magnetic change due to the disappearance of allyl double bonds only in the course of polymerisation cannot fully account for the observed higher diamagnetic susceptibility value of a polymerised product.

From the study of the double refraction of polystyrene, Signer (*Trans. Faraday Soc.*, 1936, **32**, 296) concluded that on polymerisation styrene forms long chains of rod-shaped anisotropic molecules.

Experiments on magnetic birefringence of polystyrene have shown that a definite orientation of the polystyrene molecules prevails in a manner similar to that in the liquid crystals. This orientation has a two-fold effect on the value of the diamagnetic susceptibility. A first-order-effect arises from the fact that on account of the orientation in space not all directions

are equivalent and that therefore the mean value used in the derivation of the Langevin formula $x^2 + y^2 = \frac{2}{3}r^2$ does not hold good any longer, as a result of which the factor 2/3 is to be replaced by something different. Another effect arises from the influence of the magnetic field on the electric moment of the oriented molecules which, although it is only of the second order, should be quite remarkable, since it is of the same type as the magnetic birefringence. Thus the observed susceptibility value is the net result of the magnetic changes due to the constitutional changes involved in the formation of polystyrene molecules and due to its anisotropy.

From Table II it is clear that the pull per gram for styrene heated in vacuum goes on increasing with the time of heating, but for styrene heated in presence of air, it slightly falls at first and then begins to rise and the value remains less than that for the sample heated in vacuum till the mass has been heated for 14 hours. After that the pull per gram for styrene heated in air is more than that heated in vacuum.

Staudinger and Lautensihläger (*Annalen*, 1931, **488**, 1) have shown that the polymerisation products of styrene formed in the presence of oxygen always contain small amounts of peroxide. Thus when styrene is polymerised in presence of oxygen, two reactions, oxidation and polymerisation, proceed simultaneously. The effect of polymerisation on the magnetic susceptibility of the polymerised products would be to raise its diamagnetic susceptibility as has been shown by determining the susceptibility of styrene heated in vacuum, whereas the effect of the formation of peroxide is known in general to lower the susceptibility value.

Exact susceptibility values of the polymerised products could be determined theoretically, if the percentage of the peroxide formed were known and if its susceptibility could be determined. The peroxide has, however, not been isolated.

A slight fall in the pull per gram observed in the beginning on styrene, heated in the presence of air, suggests that the susceptibility of the peroxide is much lower than that of the polymer, but as the polymerisation proceeds and the magnetic effect due to polymerisation increases, the pull per gram goes on rising. After 14 hours, the pull per gram on styrene heated in air is much more than that on the sample heated in vacuum, because the percentage of polymerisation of styrene heated in air is much higher than that heated in vacuum.

STUDIES IN DEHYDROGENATION. PART VI.

. By Suresh Chandra Sen-Gupta.

The synthesis and selenium dehydrogenation of 6 : 7-*cyclo*penteno-1 :2 :3 :4-tetra-hydronaphthalene-2 · 2-spiro-*cyclo*pentane have been described. A rational synthesis of 2 :3-*cyclo*pentenophenanthrene has also been carried out.

In order to study selenium dehydrogenation of complex spiro-hydrocarbons, 6 7-*cyclo*penteno-1:2:3 : 4-tetrahydronaphthalene-2 : 2-spiro-*cyclo*pentane has been synthesised. The anhydride of *cyclo*pentane-1-carboxy-1-acetic acid has been condensed with hydrindene, forming primarily αα-*cyclo*pentane-β-5-hydrindoylpropionic acid (I). The formation of trimellitic acid by the oxidation of this keto-acid with alkaline per-manganate proves the linking of the keto group to 5 position of the hydrindene molecule. This keto-acid on reduction by the Clemmensen method gives αα-*cyclo*pentane-γ-5-hydrindylbutyric acid (II), and the latter on cyclisation with 85% sulphuric acid gives 1-keto-6:7-*cyclo*penteno-1:2:3:4-

(I)   (II)   (III)

tetrahydronaphthalene-2:2-spiro-*cyclo*pentane (III). The course of the cyclisation of the hydrindylbutyric acid (II) in forming the linear product (III), follows from the oxidation of the latter to 1:2:4:5-benzene-tetra-carboxylic acid   The spiro-ketone (III) by Clemmensen reduction gives 6:7-*cyclo*penteno-1:2:3:4-tetrahydronaphthalene-2:2-spiro-*cyclo*pentane (IV).

(IV)   (V)   (VI)

It was expected that the spiro-hydrocarbon (IV) on selenium dehydro-genation would yield either 2:3-*cyclo*penteno-anthracene (VI) or 2:3-*cyclo*-

pentenophenanthrene (V) or both (*cf. J. Indian Chem. Soc.*, 1939, **16**, 89, 349). In order to settle the constitution of the hydrocarbon obtained by dehydrogenation, a rational synthesis of 2:3-*cyclo*pentenophenanthrene has been carried out. The dehydrogenation product is found to be different from 2:3-*cyclo*pentenophenanthrene and is in all probability 2:3-*cyclo*penteno-anthracene.

The synthesis of 2:3-*cyclo*pentenophenanthrene has been carried out in the following manner. By the Friedel-Craft's reaction of the anhydride of Δ^1-*cyclo*pentene-1:2-dicarboxylic acid and naphthalene in nitrobenzene solution, a mixture of the isomeric keto-acids (VII) is obtained, from which the isomers could not be separated in a pure condition. The mixture of the keto-acids is reduced by Clemmensen's method giving a mixture of the isomeric naphthyl acids (VIII). An attempt to cyclise the mixture with 85% sulphuric acid at 100° resulted in a very poor yield of the

(VII)   (VIII)   (IX)

cyclisation product owing to extensive sulphonation, ring-closure being ultimately effected with zinc chloride at 180°. In the latter case an excellent yield of the cyclisation product, which was evidently a mixture of (IX, R=CH₂; R'=CO; IX, R=CO; R'=CH₂) is obtained. Clemmensen reduction of the mixture of ketocyclic compounds gives a homogeneous product namely 2:3-*cyclo*penteno-1:4-dihydrophenanthrene (IX, R=R'=CH₂). Selenium dehydrogenation of this hydrocarbon in a sealed tube at 300-310° gives a good yield of 2:3-*cyclo*pentenophenanthrene. It is obtained in a crystalline condition and readily yields a picrate and a trinitrobenzene complex which are different from the corresponding derivatives obtained from the dehydrogenation product of 6:7-*cyclo*penteno-1:2:3:4-tetrahydronaphthalene-2:2-spiro-*cyclo*pentane.

EXPERIMENTAL.

αα-*cyclo*Pentane-β-5-hydrindoylpropionic Acid (I).—It was prepared from hydrindene (24 g.), anhydride of *cyclo*pentane-1-acetic-1-carboxylic acid (31 g.), aluminium chloride (52 g.) in nitrobenzene solution. The

mixture was kept in an ice-bath for 6 hours and at the ordinary temperature for 12 hours. After decomposition with ice and hydrochloric acid, excess of nitrobenzene and hydrindene were removed in steam. The solid product was extracted with sodium carbonate solution. It was crystallised first from glacial acetic acid and finally from rectified spirit in colourless needles, m.p. 140-41°. (Found: C, 74·9; H, 7·3. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·3 per cent).

The *methyl ester* distilled as a thick oil, b.p. 210-212°/5 mm., which slowly solidified on standing, m.p. 47-48°. (Found: C, 75·2; H, 7·8. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·7 per cent).

Oxidation of the Keto-acid (I).—The keto-acid (1 g.) was dissolved in sodium hydroxide (5%, 100 c.c.) solution and heated on the water-bath with excess of potassium permanganate solution. After the excess of permanganate was destroyed with alcohol, the filtrate from the precipitated manganese dioxide was acidified with hydrochloric acid and evaporated to dryness on the water-bath. It was extracted with ether, solvent removed and the residue crystallised from concentrated hydrochloric acid and identified as trimellitic acid, m.p. 214°.

αα-cycloPentane-γ-5-hydrindylbutyric Acid (II).—*αα-cyclo*Pentane-β-5-hydrindoylpropionic acid (15 g.), amalgamated zinc (75 g.) and concentrated hydrochloric acid (75 c.c.) were gently boiled for 24 hours. The product was extracted with ether, extract washed with water, solvent removed and the residue purified by distillation at 220°/6 mm. The distillate (11 g.) was crystallised from petroleum ether (b.p. 40-60°) in hexagonal plates, m.p. 104-5°. (Found: C, 79·0; H, 8·5. $C_{17}H_{22}O_2$ requires C, 79·1; H, 8·5 per cent).

6:7-cycloPenteno-1-keto-1 : 2 : 3 :4-tetrahydronaphthalene-2:2-spiro-cyclopentane (III).—The foregoing hydrindylbutyric acid (7 g.) was cyclised by heating with 85% sulphuric acid (sulphuric acid 21 c.c. and water 7 c.c.) for 1½ hours on the steam-bath. The solid product was crystallised from petroleum ether (b.p. 40-60°) in long prisms, m.p. 98-99°, yield 5·5 g. (Found: C, 85·07; H, 8·2. $C_{17}H_{20}O$ requires C, 85·0; H, 8·3 per cent).

The *oxidation of the spiro-ketone* (III) was carried out with alkaline permanganate solution as in the case of the oxidation of the keto-acid (I). The product was crystallised from concentrated hydrochloric acid in needles and after drying in the air-bath at 100° was converted into its anhydride by heating with acetyl chloride. The anhydride was identical with the di-anhydride of 1.2:4:5-benzenetetracarboxylic acid, m.p. 284°.

6:7-cycloPenteno-1 : 2 : 3 :4-tetrahydronaphthalene-2:2-spiro-cyclopentane (IV).—The spiro-ketone (III) (4 g.) was heated with amalgamated zinc

6

(20 g.) and concentrated hydrochloric acid (20 c.c.) for 24 hours. The solid product was extracted with ether, solvent removed and the residue crystallised from petroleum ether (b.p. 40-60°) in colourless cubes, m.p. 64-65°, yield 2·8 g. (Found : C, 90·4 ; H, 9·6. $C_{17}H_{22}$ requires C, 90·3 ; H, 9·7 per cent).

Selenium Dehydrogenation of the Spiro-hydrocarbon (IV).—The spiro-hydrocarbon (2·5 g.) was heated with powdered selenium (3 g.) in a metal-bath at 300-320° for 10 hours and at 340-350° for 30 hours. The product was thoroughly extracted with ether and petroleum ether. The liquid hydrocarbon obtained after distilling off the solvent, was distilled over sodium under reduced pressure when a liquid distillate (0·6 g.) was obtained. The hydrocarbon (0·3 g.) was converted into picrate in benzene solution and the dark orange picrate was crystallised from alcohol, m.p. 149-50°. (Found : C, 61·4 ; H, 3·9. $C_{23}H_{17}O_7N_3$ requires C, 61·8 ; H, 3·8 per cent).

The *trinitrobenzene complex* was prepared in benzene solution. It crystallised from alcohol in beautiful orange flakes, m.p. 128-29°. (Found: C, 63·8 ; H, 4·0. $C_{23}H_{17}O_6N_3$ requires C, 64·0; H, 3·9 per cent).

Synthesis of 2:3-cyclo*Pentenophenanthrene.*—Δ^1-cyclo*Pentene-1:2-dicarboxylic acid, required for this synthesis, was prepared from ethyl *cyclo*pentanone-2-carboxylate. The cyanohydrin of this keto-ester was prepared by the action of liquid hydrocyanic acid, and the corresponding unsaturated nitrile by dehydration with thionyl chloride. The nitrile on hydrolysis readily gave the required *cyclo*pentenedicarboxylic acid.

Cyanohydrin of Ethyl cyclo*Pentanone-2-carboxylate.*—Ethyl *cyclo*pentanone-2-carboxylate (52 g.) was added to hydrocyanic acid (obtained from 65 g. of potassium cyanide), while cooled in a freezing mixture. A drop of potassium cyanide solution was added to the mixture and left overnight. The excess of hydrocyanic acid was removed under reduced pressure at the ordinary temperature and the crude cyanohydrin mixed with dry benzene (50 c.c.) and dried with sodium sulphate.

The benzene solution of the cyanohydrin was cooled in a freezing mixture and thionyl chloride (50 c.c.) was added drop by drop with constant stirring. After leaving overnight, the mixture was heated to boiling on the water-bath for 1 hour. It was then poured into ice, benzene layer was separated and the insoluble product extracted with benzene. The benzene solution was dried with calcium chloride and distilled. The fraction, b.p. 130°-140°/8 mm. was collected and redistilled at 133-135°/4 mm., the yield of the unsaturated nitrile ester being 25 g.

Hydrolysis of the Unsaturated-Nitrile Ester.—The foregoing nitrile (20 g.) was boiled with concentrated hydrochloric acid (50 c.c.) for 2 hours, when

the oily layer disappeared. Water (50 c.c.) was added to this solution and the solution heated further for 5 hours. On cooling Δ^1-cyclopentene-1:2-dicarboxylic acid crystallised out and was recrystallised from water, m.p. 178° (lit. 178°), yield 13 g. (Found: C, 53·6 ; H, 5·2. $C_7H_8O_4$ requires C, 53·8; H, 5·1 per cent).

Anhydride of Δ^1-cyclopentene-1:2-dicarboxylic acid was obtained as a colourless liquid by boiling with acetic anhydride, b.p. 130°/5 mm.

Δ^1-cycloPentene-1-(α and β-naphthoyl)-2-carboxylic Acid (VII).—Aluminium chloride (34 g.) was added to an ice-cold solution of naphthalene (20 g.) and the anhydride of cyclopentene-1:2-dicarboxylic acid (17 g.) in nitrobenzene (100 c.c.). The product was worked up in the usual manner and after crystallisation from glacial acetic acid had m.p. 155-65°.

Clemmensen Reduction of the foregoing mixture of Keto-acids.—The mixture of the keto-acids (17 g.), amalgamated zinc (80 g.) and concentrated hydrochloric acid (80 c.c.) was heated for 18 hours. The product was obtained as a thick liquid, b.p. 215-220°/5 mm. yield 12·5 g.

2:3-cycloPenteno-1.4-dihydrophenanthrene (IX, R=R'=CH$_2$).—The mixture of the naphthyl acids (VIII) (6·5 g.) was heated with fused powdered zinc chloride (15 g.) at 180° for ½ hour, the product was treated with dilute hydrochloric acid and extracted with ether. The ether solution was washed with dilute ammonia and water and solvent distilled off. The oily residue (5 g.) was directly reduced by heating with amalgamated zinc (25 g.) and hydrochloric acid (25 c.c.) for 18 hours. The product was distilled under reduced pressure when the distillate readily solidified. It was crystallised from petroleum ether (b.p. 50-60°) in thick plates, m.p. 101-2°, yield 2·6 g. (Found· C, 92·5 ; H, 7·4. $C_{17}H_{16}$ requires C, 92·7; H, 7·3 per cent).

2:3-cycloPentenophenanthrene (V).—The foregoing hydrocarbon (2 g.) was heated in a sealed tube with selenium (2 g.) at 300-320° for 24 hours. The product was extracted with ether, solvent distilled off and the crystalline residue was distilled over sodium under reduced pressure, yield 1·6 g.

The trinitrobenzene complex was prepared from the hydrocarbon (0·3 g.) and trinitrobenzene (0·3 g.) in alcoholic solution. The additive compound crystallised from alcohol in fine yellow silky needles, m.p. 162-63°. (Found: C, 63·9 ; H, 3·9. $C_{23}H_{17}O_3N_6$ requires C, 64·0 ; H, 3·9 per cent).

The picrate crystallised from alcohol in golden yellow needles, m.p. 157°. (Found C, 61·7; H, 3·9. $C_{23}H_{17}O_7N_3$ requires C, 61·8; H, 3·8 per cent).

Pure 2:3-cyclopentenophenanthrene was regenerated from the picrate by decomposition with ammonium hydroxide. It crystallised from methyl

alcohol in stout needles, m.p. 84°. (Found: C, 93·5; H, 6·4. $C_{17}H_{14}$ requires C, 93·6; H, 6·4 per cent).

The author desires to express his grateful thanks to Dr. M.Qudrat-i-Khuda for the facilities given to him for carrying out this investigation at the Presidency College Laboratory and to Dr. J. C. Bardhan for his keen interest.

THE CHEMISTRY OF OLEO MARGOSA FROM *MELIA AZADIRACHTA* OR NEEM OIL. PART I. ISOLATION OF THE CONSTITUENTS OF THE OIL.

By Muhammad Qudrat-i-Khuda, Subash Kumar Ghosh
AND Asutosh Mukherjee.

Six different substances have been separated from the oleo margosa or the neem oil. The main odoriferous constituent of the oil is a sulphur containing liquid of the molecular formula $C_{15}H_{30}O_3S$. A glucoside, which is the bitter principle of the oil, has been isolated. The latter appears to possess the formula $C_{28}H_{48}O_{10}$. Besides the oil consists of the glycerides of four acids, two of which (A and B) are saturated and the other two (C and D) are unsaturated Of these the acid (A) (m p. 67°) appears to be an isomer of tetradecoic acid, while the acid (B) (m.p. 55°), is most probably an isomer of palmitic acid. The unsaturated acid (C, belongs to oleic acid series and possesses the formula $C_{15}H_{28}O_2$ The fourth acid (D) belongs to the cyclic series of acid of the formula $C_{18}H_{32}O_2$.

Owing to the conflicting data about the neem oil and in view of its medicinal properties, it was thought necessary to put the oil as well as other portions of the tree to a closer examination.

Genuine samples of neem oil in quantity used in this investigation were procured from Birbhum, where the cultivators collect the seeds late in summer and then get them pressed for their own use as an insecticide and a fuel.

The physical data more or less agreed with those given by Chatterjee and Sen (*Indian J. Med. Res.*, 1920, **8**, 356). It contains a volatile odoriferous constituent together with a very bitter substance. These substances have now been isolated in fairly pure condition. Chatterjee (*Indian J. Med. Res.*, 1917-18, **5**, 656) attempted to free the oil of its odour by steam distillation and subsequently saponified it. The acid, isolated by him, must have contained the bitter principle. Chatterjee and Sen (*loc. cit.*) did not recognise that the bitter principle and the fatty acids in the oil might be independent of each other. Watson, Chatterji and Mukherji (*J. Soc. Chem. Ind.*, 1923, **42**, 387T) attempted the separation of the different ingredients. But the method adopted by them did not appear to us to be very suitable.

The oil on keeping develops a rancid odour. It was, therefore, worked up very soon after receiving it from the source. It was first subjected to a process

of prolonged steam distillation until all volatile substances were removed. This distillate consisted of the odoriferous constituent of the oil mixed with a small quantity of a solid substance   This oil, however, on repeated distillation, was obtained as a colourless mobile liquid with a very penetrating and extremely unpleasant odour. This oil, designated as* *Neemola,* contains sulphur. Analytical data and molecular weight suggest its molecular formula as $C_{15}H_{30}O_3S$. From about 30 lb. of crude neem oil only 15 g. of Neemola could be obtained. Further work on its constitution is now in progress.

The residue after steam distillation still possessed rather an unpleasant odour which was not quite as marked as that of the original oil. This oil was next extracted 5 to 6 times with water. The aqueous solution obtained from the residue of steam distillation was found to be extremely bitter, while the steam distillate, although possessed a highly obnoxious smell, did not taste bitter at all. The bitter principle was, therefore, present in the residual oil. On extracting it continuously with several litres of water, it was rendered far less bitter than the original oil. This aqueous solution yielded a mixture of a solid together with a little oil but the separation was not difficult. The bitter constituent of neem oil was thus obtained as a solid which has been called " Margosin". This was purified, analysed and found to be free from sulphur, thus differing from the observations of Sen and Banerji (*J. Indian Chem. Soc.,* 1931, **8,** 773). It analysed for a glucoside of the formula $C_{28}H_{48}O_{10}$. The degradation experiments with Margosin are now in progress.

The fatty oil remaining after the separation of neemola and margosin was saponified and from the potassium soap a mixture of four acids could be separated which appeared to be different from those of Roy and Dutt (*J. Soc. Chem. Ind.,* 1929, **48,** 333T) and Child and Ramanatham (*ibid.,* 1936, **55,** 124T). One of these acids melted at 67° but was found to be different from stearic acid. From analysis and molecular weight, it appears to be an isomer of tetradecoic acid of the formula $C_{14}H_{28}O_2$ which we have called. Neem Acid " A". Together with this acid another solid acid was isolated which melts at a lower temperature, *viz.,* 55°, but appeared to be a higher homologue of acid " A". Its analysis and molecular weight suggested it to be an isomer of palmitic acid, $C_{16}H_{32}O_2$; this we have called Neem Acid " B". Hilditch and Murti (*J. Soc. Chem. Ind.,* 1939, **58,** 310) also isolated some acids; their observations are similar to those of Roy and Dutt (*loc. cit.*). It appears to us that the earlier workers were misled by the physical properties of the acids because we do not find any analytical data regarding the acids from the papers of these authors.

After the separation of the two solid acids, the mother-liquor still contained some acidic substance, which solidified on cooling. The acid was, therefore, distilled under reduced pressure when it was obtained as a mixture of a solid and an oily substance which could be mechanically separated.

This oily mixture of acids was, therefore, esterified. The methyl ester was fractionated into two distinct portions. Both the esters are unsaturated and from them two acids could be regenerated. The lower boiling ester, $C_{16}H_{30}O_2$ (the ester of the neem acid C) absorbs bromine giving a dibromo derivative, which decomposes partially on distilling under reduced pressure. The free acid generated from the ester was isolated as a solid after distillation. It appears to possess the formula $C_{15}H_{28}O_2$ and thus belongs to the oleic acid series.

The higher boiling ester, $C_{19}H_{34}O_2$, give a dibromo derivative which also decomposes partially on distillation. From it, the acid $C_{18}H_{32}O_2$, isolated after hydrolysis, solidified partially at the ordinary temperature on standing for some time. This has been called Neem Acid "D", and apparently belongs to the cyclic series of acids perhaps similar to hydnocarpus or chaulmoogric acids. These acids are under investigation.

E X P E R I M E N T A L.

The oil that was obtained from the market was filtered and the physical properties were determined. It was found to have $d_4^{22 \cdot 9} = 0 \cdot 9108$ and $n_D^{22 \cdot 9}$, $1 \cdot 46185$. Its iodine value was found to be $69 \cdot 56$ and saponification value, $198 \cdot 8$.

Neemola (Odoriferous Constituent of Neem Oil).—Neem oil (220 g.) was subjected to steam distillation (sand-bath being replaced by a water-bath to prevent decomposition of the active principle). Some oily globules together with some solid particles distilled over with steam. After six litres of distillate were collected, no further oily globules came over with steam. The distillate from 1 kg. of oil was cooled in ice and saturated with ammonium sulphate and extracted three times with ether. The ethereal extract, dried over magnesium sulphate, furnished after removal of solvent a pungent and nauseous smelling light yellow liquid. The oil was carefully and slowly distilled under reduced pressure from a glycerine-bath, the receiver being cooled in a freezing mixture. The first fraction collected at $150\text{-}60°/110$ mm. was a light brown mobile liquid with the most acrid smell. On redistillation it had b.p. $156\text{-}58°/118$ mm. [Found: C, $61 \cdot 94$; H, $9 \cdot 81$; S, $10 \cdot 86$; M.W. (cryoscopic in benzene), $289 \cdot 3$. $C_{15}H_{30}O_3S$

requires C, 62·2; H, 10·3; S, 11·07 per cent. M.W., 290]. It is distinctly acidic being soluble in sodium carbonate solution from which it is reprecipitated on acidification. It immediately decolourises bromine but is not bitter in taste. It gives no ferric chloride reaction.

The second fraction, collected at 200-210°/7 mm., was a thick viscous mass and solidified on keeping. The solid crystallised from petroleum ether and proved identical with neem acid " B " (vida supra).

Margosin (the Bitter Principle of Neem Oil).—The solution left with oil after steam distillation, tasted very bitter. This was mixed with aqueous extract of the oil with water (5 times) and then examined for the bitter principle. But subsequently it was found better to extract the oil by a continuous process with hot water. The aqueous extract was evaporated to dryness under reduced pressure. The oily brown residue, which was extremely bitter, was triturated with petroleum and then extracted with hot chloroform. The chloroform solution was then thoroughly washed with sodium bicarbonate solution (10%). It was then charcoaled for $\frac{1}{2}$ hour. The chloroform was removed on the water-bath when a light yellow amorphous mass was obtained, which was further purified by washing with hydrochloric acid solution and then by precipitation from ether solution with petrol. The purified sample was obtained as a light yellow amorphous powder, m.p. 193-95° (decomp). [Found : C, 62·01 ; H, 8·91 ; M.W. (ebullioscopic), 575. $C_{28}H_{48}O_{10}$ requires C, 61·76 ; H, 8·8 per cent. M.W., 544]. It is neutral in reaction and reduces Fehling's solution after hydrolysis with hydrochloric acid. It is probably a glucoside. We designate it as margosin. It shows no reaction with bromine in chloroform solution and does not give ferric chloride reaction.

Isolation of the Acids A, B, C and D from Neem Oil.—200 G. of the oil were hydrolysed on a gently boiling water-bath with 100 g. of potassium hydroxide in 450 g. of aqueous alcohol for 10 hours. The thick viscous material was cooled and was treated with water, when the potassium salts separated out as solid mass. These were collected, washed with cold water and subsequently acidified in aqueous suspension when a semi-solid mass of mixture of acids separated out. These were collected after cooling. On standing the precipitate became oily and the oily portion was freed at the pump as far as practicable. The solid residue was then triturated with petroleum ether, cooled at about 25° and then filtered. The filtrate on dilution with more petroleum and cooling to below 10°, gave some solid acids.

The crystalline solid acid mixture was triturated with just enough petroleum to give a thin paste, then cooled to about 25° and filtered by suction,

when the solid could be freed from most of the oily matter. But it was necessary to repeat the process several times before a complete separation could be effected. The solid residue was further purified by recrystallisation from petroleum when it had m.p. 67°. [Found : C, 74·21 ; H, 12·02 ; M.W. (ebullioscopic), 240; M.W. (by titration for a monobasic acid), 232·4. $C_{14}H_{28}O_2$ requires C, 73·7; H, 12·2 per cent. M.W., 228].

The petroleum mother-liquor from the solid acid on cooling to 15° gave a second acid which melted at 50-53°. The filtration must be rapid otherwise the acid dissolves in the solvent with rise of temperature. This was purified by several crystallisations. Depending on dilution some times the solution was cooled to about 4-5°, before it crystalliseed. The purified acid "B" melts at 55°. [Found : C, 75·3 ; H, 12·2 ; M.W. (ebullioscopic), 260·2; M.W. (by titration, for a monobasic acid), 256·7. $C_{16}H_{32}O_2$ requires C, 75·0 ; H, 12·5 per cent. M. W., 256].

Separation of the Oil "X".—The oily product consisted of a mixture of two acids only. After removal of the solvent from the dried solution, the acid mixture (50 g.) was mixed with methyl alcohol (200 c.c.) and sulphuric acid (10 c.c., d 1·84) and esterified. The methyl alcoholic solution of the acids separated into two layers as soon as sulphuric acid was added. The mixture was heated on the steam-bath for about 7 hours when the layers practically disappeared. After removal of methanol and addition of water, the oily ester layer was purified in the usual way and distilled. The first fraction was collected at 205°/14 mm. and second at 215°/14 mm. After several redistillations the methyl ester of neem acid "C" had b.p. 177°/3 mm. [Found : C, 76·03; H, 11·7. M.W. (cryoscopic), 254. $C_{16}H_{30}O_2$ requires C, 75·6; H, 11·8 per cent. M.W., 253]. It had $d_4^{32·4}$, 0·84801; $n_D^{32·4}$, 1·43781, whence $[R_L]_D$ found : 78·28 (calc. 78·36) The ester absorbs bromine very rapidly. The bromo-ester, b.p. 230°/4 mm (decomp.) gave low halogen values. (Found : Br, 31·4. $C_{16}H_{30}O_2Br_2$ requires Br, 38·4 per cent).

The neem acid "C", isolated by hodrolysis of the methyl ester, had b.p. 189-90°/4 mm. and m.p. 47-48°. [Found : C, 75·2, H, 11·57 ; $C_{15}H_{28}O_2$ requires C, 75·03; H, 11·66 per cent. Found : Ba, 22·13. $(C_{15}H_{27}O_2)_2Ba$ requires Ba, 22·3 per cent].

The second fraction (the methyl ester of neem acid D), on redistillation had b.p. 185°/3 mm. [Found : C, 77·5; H, 11·6. M.W. (cryoscopic) 302·9. $C_{19}H_{34}O_2$ requires C, 77·6; H, 11·3 per cent. M,W., 294]. It had $d_4^{32·5}$, 0·86557; $n_D^{32·5}$, 1·44395, whence $[R_L]_D$ found : 89·57 (calc. 88·81) The ester rapidly absorbs one molecule of bromine and this bromo derivative also decomposes partially on distillation at 223°/4 mm. (Found : Br, 27·4. $C_{19}H_{34}O_2Br_2$ requires Br, 35·2 per cent).

The neem acid " D ", isolated by hydrolysis, had b.p. 194-95°/4mm. and partially crystallised on standing, the crystals had m.p. 31-33°. [Found: C, 77·01; H, 11·7. $C_{18}H_{32}O_2$ requires C, 77·14; H, 11·43 per cent. Found: Ba, 19·3. $(C_{18}H_{31}O_2)_2$ Ba requires Ba, 19·7 per cent]. This acid also rapidly absorbs bromine at the ordinary temperature.

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ELECTRODIALYSIS OF SOILS. THE INFLUENCE OF EXCHANGEABLE BASES ON THE RECOVERY OF MANGANESE BY ELECTRODIALYSIS.

By R. C. Hoon and C. L. Dhawan.

Soils containing manganese and one of the elements viz., Na, K, Ca and Mg were electrodialysed and the manganese, both in the electrodialysate and the deposit on the cathode etc., was separately determined. As the result of this study, the effect of different bases which may be present in the exchange complex of soils on the recovery of manganese is brought out.

A few natural soils have been subjected to electrodialysis and the manganese in the electrodialysate determined. Bad soils yield greater amount of manganese in the electrodialysable form than soils with low p_H values.

It is concluded that at high p_H values when, the dominant base in the exchange complex of soils is sodium, more manganese comes out in the soluble form and is thus made available to plants. This availability of mangenese to plants may be reduced when the dominant base in the exchange complex of soils is calcium or magnesium.

The importance of trace elements in the soil in influencing plant nutrition is gradually being realised. It is well known that replaceable or electrodialysable bases are more readily available to plants than the non-replaceable ones. The estimation of these bases by electrodialysis has been recommended by several workers (S. Mattson, *Soil Sci.*, 1938, **45**, 309 ; Prince and Toth, *ibid.*, 1938, **46**, 83 ; Puri and Hoon, *ibid.*, 1936, **43**, 305). This method has been recently applied to study the antagonism between sodium and calcium in soils (Puri, Hoon and Dhawan, *Soil Sci.*, 1939, **47**, 479). As the replaceable bases appear as hydroxides on electrodialysis, manganese occupies a peculiar position in so far as its hydroxide is sparingly soluble in water. Thus not only it will have a tendency to be deposited on the cathode but the presence of other bases will exercise an influence on the manner of its recovery by electrodialysis. Prince and Toth (*loc. cit.*) by using soils partially saturated with manganese, recently studied the effect of lime on exchangeable and electrodialysable manganese. They found that with the increase of lime applications the exchangeable manganese decreased.

The object of the present investigation was to study the extent to which the recovery of manganese from soils by electrodialysis might be affected by the presence of other bases in the exchange complex.

EXPERIMENTAL.

Preparation of Soils.

(*i*) Three soils were selected for this study. Soil No. P.C. 13 was a black cotton soil of high exchange capacity. Soil No. P.C. 72 was an alluvial clayey loam and soil No. P.C. 123 was a raw alluvial clayey sub-soil containing 83 % of clay. The following table gives the mechanical composition of these three soils.

TABLE I.

Soil No.	Sand.	Silt.	Clay (particles) below 0·002 mm.
P. C. 13	23·55 %	20·65 %	53·30 %
P. C. 72	4·52	49·75	44·08
P. C. 123	6·20	10·60	83·20

The soils were leached with 0·05N-HCl exhaustively to remove the exchangeable bases and then washed with distilled water until free from chlorides.

FIG. 1.

Titration curves of H-soil prepared from P.C. 13.
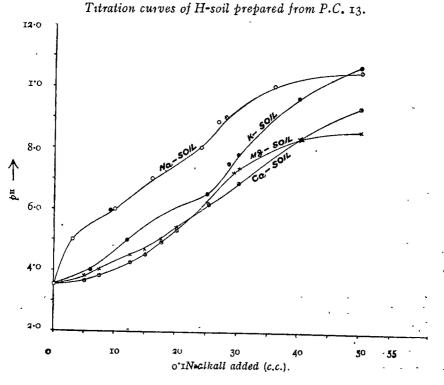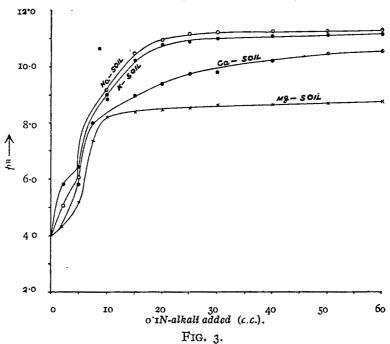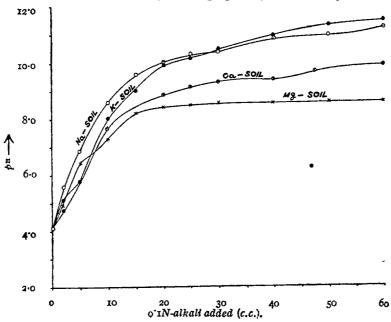
FIG. 2.

Titration curves of H-soil from P.C. 72.

FIG. 3.

Titration curves of H-soil prepared from P.C. 123.

Figsures 1-3 give the titration curves of the H-soils, thus obtained, with hydroxides of Na, K, Ca and Mg and show that the soils differ widely as regards their behaviour towards bases.

(*ii*) The H-soils, obtained above, were converted to manganese soils by treating 50 g. portions with a litre of normal manganese chloride solution according to Prince and Toth (*loc. cit.*). The soils were then washed free of chlorides.

(*iii*) To 5 g. portions of the manganese soils, hydroxides of Na, K, Ca and Mg were added separately in increasing amounts. In this way sets of manganese soils containing varying amounts of each one of the four bases and having different p_H values were obtained. The soils were shaken with distilled water for 48 hours before subjecting them to electrodialysis.

Equipment and Technique of the Method used for Electrodialysing Soils.

The electrodialysis of soils was carried out for 5 hours at 100 milliamp. current in an apparatus fitted with a rotating anode and a cone-shaped cathode made from thick platinum gauze. Formerly (Puri and Hoon, *loc. cit.*; *Soil Sci.*, 1938, **45**, 309) a copper cone served as the cathode. It was, however, found that on electrodialysing manganese soils some material was deposited on the cathode and the filter paper holding the suspension. In this investigation it was therefore considered necessary not only to determine the manganese content of the electrodialysate but also of the deposit on the cathode etc.

The electrodialysate was titrated with standard HCl using phenolphthalein as indicator and then manganese was determined by the bismuthate method (*Imp. Bureau Soil Sci. Bull.*, 1937, No. 17). The deposit on the cathode and filter paper (after washing off the soil suspension) was dissolved in dilute H_2SO_4 and its manganese content determined separately as in the electrodialysate. The amount of manganese actually removed by electrodialysis of soils is represented by the total of the mangenese determined in the electrodialysate and the deposit on the cathode etc.

The p_H of 1:5 soil-water suspensions, given in the tables was determined by the glass electrode (Hoon and Taylor, *Memoir Punj. Irri. Res. Inst.*, **4**, No. 1).

It was considered of interest to determine the manganese content of artificially prepared manganese soils by different methods and compare the results. The manganese content of the soils, prepared from the three soils

described under (a) (ii) prior to the addition of the hydroxides of Na, K, Ca and Mg was determined by the following methods:

(i) Directly from the manganese soils by bismuthate method.

(ii) Leaching the soils with neutral ammonium acetate and estimating manganese in the leachates.

(iii) Subjecting the soils to electrodialysis and determining manganese in the electrodialysate and the deposit on the cathode, etc. separately. The results are given in Table II.

TABLE II.

Manganese content of artificially prepared manganese soils by different methods.

Manganese soil prepared from soil No.	p_H of 1:5 soil-water suspension.	Total manganese content (direct).	Manganese in N-ammonium acetate leachate of soils.	Mn recovered by electrodialysis in 5 hr.		
				(A) in the electrodialysate.	(B) deposited on the cathode.	(A + B)
P. C. 13	3·62	63·75 m. eq.	44·60 m. eq.	10·9 m. eq.	10·6 m. eq.	21·5 m. eq.
P. C. 72	4·80	41·75	35·80	11·6	11·9	23·5
P. C. 123	4·14	31·80	22·40	20·8	10·6	31·4

DISCUSSION.

The results show that whereas in manganese soils prepared from P. C. 13 and P. C. 72, only a portion of the total manganese could be recovered on electrodialysing for 5 hours, the amount being even less than that recovered by leaching the soils with normal ammonium acetate solution, almost the whole of manganese was recovered by electrodialysis from manganese soil prepared from P. C. 123. These differences in the recovery of manganese from the three soils are rather significant. In manganese soils, prepared from P. C. 123, the recovery of manganese by electrodialysis is quick and almost complete in 5 hours under the conditions of the experiment. With manganese soils prepared from P.C. 123 and P. C. 72, however, the recovery of manganese is a much slower process.

TABLE III.

Electrodialysis of soils artificially prepared from P.C. 13.

Base added to the manganese soil.	p_H of 1 : 5 soil-water suspension.	Manganese recovered by electrodialysis from soils.		Total.	Recovery of the other base.
		Mn present in the elec-trodialysate.	Mn present in the depo-sit.		
		Mn-Na soils.			
4·0 m. eq.	5·49	8·40 m. eq.	15·60 m. eq.	24·00 m. eq.	52·5 %
10·0	7·29	4·50	9·60	14·10	80·0
26·0	8·18	5·60	8·20	13·80	89·2
50·0	10·12	14·50	—	14·50	82·4
100·0	11·00	15·20	—	15·20	70·9
		Mn-K soils.			
4·0	5·31	7·00	15·40	22·40	75·0
10·0	6·80	4·70	12·70	17·40	79 0
26·0	8·29	6·10	11·90	18·00	85·7
50·0	9·60	3·00	3·40	6·40	78·6
100·0	10·08	4·40	3·40	7·60	94·0
		Mn-Ca soils.			
15·0	5·62	14·80	17·60	32·40	35·3
20·0	6·56	9·70	9·90	19·60	33·5
25·0	6·86	11·80	7·10	18·90	48·4
37·0	7·26	3·80	4·50	8·30	44·0
50·0	7·82	5·40	1·90	7·30	40·0
90·0	8·55	5·10	2·10	7·20	45·4
		Mn-Mg soils.			
10·0	5·80	8·70	5·00	13·70	3·0
30·0	6·34	5·10	16·20	21·30	3·3
60·0	7·33	2·00	18·90	20 90	5·16
130·0	8·25	2·30	19·60	21·90	4·40

TABLE IV.

Electrodialysis of artificially prepared soils from P. C. 123.

Base added to the manganese soil.	p_H of 1:5 soil-water suspension.	Manganese recovered by electrodialysis.			Recovery of the other base.
		Mn recovered in the electro-dialysate.	Mn recovered in the deposit on the ca-thode.	Total.	
		Mn-Na soils.			
4·0 m. eq.	6·30	16·60 m.eq.	—	16·60 m. eq.	100·0 %
20·0	7·76	10 00	6·00 m. eq.	16·0	100·0
30·0	9·14	11·40	2·60	14·0	100·0
50·0	9·90	12·20	3·80	16·0	100·0
100·0	10·14	9·80	2·00	11·80	94·3
		Mn-K soils			
4·0	6·04	18·40	5·20	23·60	100·0
20·0	7·05	14·80	4·00	18·80	99·5
30·0	8·22	13·60	4·40	18·00	96·0
50·0	10·12	7·20	2·70	9·90	97·4
100·0	10·52	10·60	1·10	11·70	98·7
		Mn-Ca soils.			
4·0	5·04	13·40	1·90	15·30	92·5
10·0	6·24	10·00	3·80	13·80	80·0
20·0	7·02	8·80	2·80	11·60	79·0
70·0	8·47	7·10	1·40	8·50	80·42
100·0	9·09	6·10	2·60	8·70	78·80
150·0	9·76	3·30	2·10	5·40	64·47
		Mn-Mg soils.			
10·0	5·24	6·30	11·10	17·40	38·0
30·0	6·80	9·10	7·30	16·40	21·0
50·0	7·70	5·40	10·50	15·90	20·6
80 0	7·90	6·00	8·60	14·60	19·25
150·0	8·15	5·00	8·60	13·80	14·0

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TABLE V.

Electrodialysis of artificially prepared soils from P.C. 72.

Base added to the manganese soil.	p_H of 1:5 soil-water suspension.	Manganese recovered by electrodialysis.			Recovery of the other base.
		Mn recovered in the electro-dialysate.	Mn deposited on the ca-thode.	Total.	
		Mn-Na soils.			
4·0 m. eq.	7·40	12 20 m. eq.	4·60 m. eq.	16·80 m eq.	97·5 %
10·0	8·56	9·80	2·80	12·60	100·0
20·0	9·06	7·80	4·40	12·20	97·0
50·0	11·10	8·80	1·00	9·80	95·2
100·0	11·25	7·50	2·00	9·50	99·8
		Mn-K soils.			
4·0	7·10	9·20	4·60	13·80	100·0
10·0	7·90	10·50	5·20	15·70	100·0
20·0	9·20	6·80	2·80	9·60	100·0
50·0	11·45	3·00	0·20	3·20	94·4
100·0	11·90	5·00	0·40	5·40	97·7
		Mn-Ca soils.			
10·0	7·48	11.20	7·00	18·20	80·0
20·0	8·30	8·50	2·80	11·30	86·0
30·0	9·00	6·60	6·20	12·80	90·0
50·0	9·96	5·10	6·50	11·60	89·8
100·0	10.54	4·30	6·40	10·70	83·6
		Mn-Mg soils.			
10·0	6·60	10.60	10·60	21·20	24·0
30·0	7·22	9·40	11·50	20·90	22·0
50·0	7·65	8·60	12·40	21·00	15·0
70·0	7·80	6·60	16·00	22·60	13·15
120·0	8·20	1·20	19·40	20·60	15·75

Tables III-V give the percentage recoveries of manganese and the second base, on electrodialysis, from Mn-Na, Mn-K, Mn-Ca and Mn-Mg

sets of soils of varying p_H values prepared as described before (a, iii). There are again certain differences in the total manganese recovered from the various sets prepared from the three soils which are analogous to the differences obtained with pure manganese soils (Table II). There are, however, certain fundamental differences in the recovery of manganese in the electrodialysate and the deposit in the different sets of soils. The differences observed may be considered under the following heads.

Recovery of Manganese in the Electrodialysate.

(i) The maximum recovery of manganese in the electrodialysates is obtained from the Mn-Na sets of soils and on the whole there is a tendency for greater recovery of manganese with increase in p_H value.

(ii) The Mn-K and Mn-Ca sets of soils behave somewhat similarly and in these the recovery of manganese decreases as the p_H increases.

(iii) The recovery is a minimum in the Mn-Mg sets of soils.

Recovery of Manganese as Deposit.

(i) The deposit obtained on electrodialysing Mn-Na sets of soils contains the least amount of manganese and there is a tendency for the amount of manganese present in the deposits to decrease with increase in p_H value. Mn-K sets of soils behave in a similar manner to the Mn-Na sets.

(ii) The Mn-Ca sets of soils behave in a peculiar way. There is a decrease in the manganese content up to about p_H 8·0 after which there is again a slight increase.

(iii) In the Mn-Mg sets of soils the major portion of the manganese recovered by electrodialysis is present in the deposit portion.

It may be concluded from the foregoing that at high p_H values when the dominant base in the exchange complex is sodium more manganese comes out in the soluble form. With increase of the lime status of soils, on the other hand, the amount of manganese which comes in solution is greatly reduced.

Electrodialysis of Natural Soils.

The recovery of manganese from natural soils on electrodialysis was examined. A few soils from good and bad areas containing different amounts of total manganese were electrodialysed for 5 hours under conditions similar to those for artificially prepared manganese soils. Manganese was determined separately in the electrodialysate recovered in the first hour and the collective electrodialysate of the next four hours. This was done to obtain some idea as to the rate of recovery of manganese from these

soils. The manganese contents of the two portions were added together, to obtain the total recovery during five hours and its percentage on the total manganese present in the soils calculated. The results are given in Table VI.

TABLE VI.

Percentage recovery of manganese from natural soils by electrodialysis.

Reg. No. of soil.	Total manganese content.	p_H.	Manganese recovered from soil by electrodialysis.			Electrodialy. sable and total manganese.
			1st hour.	Next four hours.	Total in 5 hours.	
Good soils.						
1290	0·75 m. eq.	7·98	Nil	Nil	Nil	—
1291	1·05	7·94	Nil	Nil	Nil	—
1308	1·30	7·77	0·05 m. eq.	Nil	0·05 m. eq.	3·84 %
Bad soils.						
513	4·00	10·46	0·20	Nil	0·20	5·0
514	4·00	10·44	0·20	0 05 m. eq.	0·25	6·25
515	3·40	10·40	0·10	0·05	0·15	4·41
516	2·70	10·28	0·20	Nil	0·20	7 41

The results show that soils having high p_H values (and also high manganese contents) yield more manganese on electrodialysis than soils with low p_H values (and low manganese contents). Moreover the major portions of the electrodialysable manganese comes in the first hour of electrodialysis.

It is not surprising, therefore, that in soils of high p_H values more manganese might come out in the soluble form and thus be made available to plants. This availability of manganese may be reduced when the dominant base in the exchange complex of soils is calcium.

ON THE MOLAR ZERO FLUIDITY VOLUMES OF SOME ORGANIC COMPOUNDS.

By Amritansu Sekhar Chakravarti.

Newton Friend has shown that the quantity V_0, the molar volume at zero fluidity is an additive function of atoms and linkages in a large number of compounds. He has calculated the atomic and structural constants for some atoms and linkages. The present work is an extension of the above to nitrogen, chlorine, bromine, iodine and the co-ordinate link with an increase in co-valency (associated hydroxylic compounds) The atomic or linkage constants found for these are 6·0, 18·0, 23·0, 29·0 and 6·6 res pectively.

Newton Friend (*Trans. Faraday Soc.*, 1938, **34**, 813) derived the relationship $\phi = k(v^{\frac{8}{3}} - v_0^{\frac{8}{3}})$ between fluidity (ϕ) and specific volume (v) of a liquid, v_0 denoting the extrapolated specific volume of the supercooled liquid at the extrapolated temperature of zero fluidity or infinite viscosity This is based on the assumption that the molecules are spherical and that the attractive force between the molecules varies inversely as the eighth power of the distance between their centres. The quantity Mv_0 or V_c (M = molecular weight), termed the molar zero fluidity volume, was shown to be an additive function of atoms and linkages in the molecule, and some atomic and structural constants were evaluated (*loc. cit.*).
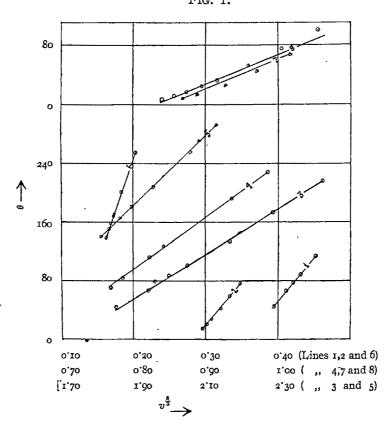
The present work is an extension of the above to nitrogen and halogen compounds, simple co-ordinate linkages and to co-ordinate linkages accompanied by an increase in co-valency of hydrogen from one to two as in the case of associated hydroxylic compounds. By analysing the viscosity and density data available, values of V_0 were arrived at (given in Table I and the following atomic constants evaluated :—

N, 6·0; Cl, 18·0; Br, 23·0; I, 29·0.

A simple co-ordinate linkage has the same value as the ordinary double bond, as would appear from the values for nitrobenzene and the nitro-toluenes.

Figure 1 shows the extent of validity of the equation, $\phi = k(v^{\frac{8}{3}} - v_0^{\frac{3}{3}})$. Lines 1 to 6 exhibit the kind of discrepancy ($\phi_{obs.} - \phi_{calc.}$) found in most

substance. Generally the discrepancies are very small. In case of *o-, m-* and *p*-phenitidine, *o*-bromoanline and *m*-toluidine. the discrepancies are greater, *o-* and *m*-phenitidine (lines 8 and 7 in the figure) showing the largest discrepancies. In case of *o*-phenitidine (line 8) the discrepancy goes up to almost 100 per cent at the lowest temperature. But, it has to be borne in mind that the value of ϕ itself is very small at this temperature and consequently a small experimental error would be enormously magnified when calculated in the form of percentage error. Even if the compounds showing large discrepancies are left out of account, there is no appreciable change in the calculated atomic constants.

FIG. I.

0·10	0·20	0·30	0·40 (Lines 1,2 and 6)
0·70	0·80	0·90	1·00 (,, 4,7 and 8)
[1·70	1·90	2·10	2·30 (,, 3 and 5)

$$v^{\frac{2}{3}} \longrightarrow$$

Line 1 refers to *o*-bromotoluene   Line 2 refers to *m*-bromoaniline

,, 3   ,,   tri-*n*-butylamine   ,, 4   ,,   *o*-chlorotoluene

,, 5   ,,   methyl alcohol   ,, 6   ,,   ethyl iodide

,, 7   ,,   *m*-phenitidine   ,, 8   ,,   *o*-phenitidine

TABLE I.

Substance	Mol. formula	k	$V_{0(obs.)}$ *	$V_{0(calc.)}$ **	% Diff
Nitrobenzene	$C_6H_5NO_2$	672·7	97·5	97·9	+0·4
Aniline	C_6H_7N	446·5	89·0	88·1	−1·0
m-Toluidine	C_7H_9N	507·8	105·0	105·1	0·0
o-Nitrotoluene	$C_7H_7O_2N$	638·0	113·3	114·9	+1·3
m-Nitrotoluene	$C_7H_7O_2N$	698·0	114·4	114·9	+0·4
o-Phenitidine	$C_8H_{11}ON$	382·3	127·9	130·1	+1·7
m-Phenitidine	$C_8H_{11}ON$	400·0	129·3	130·1	+0·6
p-Phenitidine	$C_8H_{11}ON$	375·0	129·1	130·1	+0·7
n-Triamylamine	$C_{15}H_{33}N$	229·7	277·0	273·3	−1·3
isoTriamylamine	$C_{15}H_{33}N$	242·0	279·9	273·3	−2·4
Tri-n-butylamine	$C_{12}H_{27}N$	313·0	227·7	222·3	−2·4
Diethyl ammonium picrate	$C_{10}H_{14}O_7N_4$	305·9	228·8	232·0	+1·4
Di-n-butyl ammonium picrate	$C_{14}H_{22}O_7N_4$	163·3	301·8	300·0	−0·6
Tri-n-butyl ammonium picrate	$C_{18}H_{30}O_7N_4$	278·6	367·9	368·0	0·0
Tetra-n-butyl ammonium picrate	$C_{22}H_{38}O_7N_4$	133·3	424·0	436·0	+2·7
n-Cetyl ammonium picrate	$C_{22}H_{38}O_7N_4$	41·7	444·1	436·0	−1·8
Di-n-cetyl ammonium picrate	$C_{38}H_{70}O_7N_4$	58·8	728·0	708·0	−2·8
o-Chlorotoluene	C_7H_7Cl	732·9	109·0	108·9	−0·1
m-Chlorotoluene	C_7H_7Cl	711·1	109·2	108·9	−0·2
p-Chlorotoluene	C_7H_7Cl	720·0	109·5	108·9	−0·5
Ethyl bromide	C_2H_5Br	2242·6	62·8	61·1	−2·7
o-Bromotoluene	C_7H_7Br	1206·5	116·5	113·3	−2·3
m-Bromotoluene	C_7H_7Br	1246·6	110·1	113·3	+2·3
p-Bromotoluene	C_7H_7Br	1246·6	110·1	113·3	+2·3
o-Bromoaniline	C_6H_6NBr	1253·8	107·4	106·2	−1·1
m-Bromoaniline	C_6H_6NBr	1175·4	107·2	106·2	−0·9
Methyl iodide	CH_3I	4214·3	49·5	50·2	+1·4
Ethyl iodide	C_2H_5I	2711·1	68·6	67·2	−2·0
n Propyl iodide	C_3H_7I	2000·0	85·5	84·2	−1·5
isoPropyl iodide	C_3H_7I	1929·8	86·7	84·2	−3·0

* Obtained from density and viscosity data.

** Calculated with the constants derived by Newton Friend and by the author.

The agreement is fairly good except in a few cases where the difference rises up to nearly 3%.

It appeared worth while to examine the case of a few associated liquids (co-ordination with increase in co-valency). Data on viscosity and density could be obtained for methyl alcohol (0-60°), ethyl alcohol (0-70°), n-propyl alcohol (0-90°) and acetic acid (20-110°). Throughout the temperature ranges shown against them, the plot of ϕ against $v^{\frac{8}{3}}$ gave a straight line for each of the liquids. This indicates the constancy of their degree of association over these ranges, as is well known from other considerations (Prasad, *J. Indian Chem. Soc.*, 1934, **12**, 913). $V_{0(obs.)}$ and $V_{0(calc.)}$ for these liquids, as obtained from their normal molecular weights (corresponding to ordinary chemical formulae) are given in Table II.

TABLE II.

Substance	Mol. formula	k.	$V_{0(obs.)}$	$V_{0(calc.)}$	% Diff.
Methyl alcohol	CH_4O	476·0	37·4	33·2	−12·6
Ethyl alchol	C_2H_6O	300·0	54·9	50·2	−9·4
n-Propyl alcohol	C_3H_8O	264·7	71·7	67·2	−6·3
Acetic acid	$C_2H_4O_2$	566·0	53·5	51·0	−5·0

It is seen that there is a large percentage difference in every case, the calculated values being always much lower than the observed values. Taking into account the actual molecular weights of the liquids as obtained from their degrees of association over these temperature ranges (calculated by the Eötvos-Ramsay method ; Prasad, *(loc. cit.)*, new values for V_0 could be obtained. The next problem was to see if a constant corresponding to a co-ordinate linkage with simultaneous increase in the co-valency of hydrogen existed. The method applied to test this is illustrated in the case of methyl alcohol. Methyl alcohol (CH_4O) is 3·6 or nearly 4 times associated. The molecular weight is 4×32 or 128. Four molecules are held by three co-ordinate linkages involving an increase in the co-valency of hydrogen; thus—

$$\underset{H-O}{\overset{CH_3}{\diagup}}\longrightarrow \underset{H-O}{\overset{CH_3}{\diagup}}\longrightarrow \underset{H-O}{\overset{CH_3}{\diagup}}\longrightarrow \underset{H-O}{\overset{CH_3}{\diagup}}$$

The molecular formula can be written as $(CH_4O)_4$ or $C_4H_{16}O_4$. $V_{0(obs.)}$ corresponding to $C_4H_{16}O_4$ is obtained by multiplying v_0 by the molecular weight corresponding to $C_4H_{16}O_4$. Substracting from $V_{0(obs.)}$ the sum of

the atomic constants corresponding to the above formula, we get the value for three such co-ordinate linkages to be 16·8. Hence, the value of the constant corresponding to one such co-ordinate link is 5·6. The same method is applied for finding out the constant for a co-ordinate link with simultaneous increase in co-valency of hydrogen in the cases of ethyl alcohol, n-propyl alcohol and acetic acid. The mean value of the constant is found to be 6·6. The difference in the values for a co-ordinate linkage with and without increase in co-valency has its parallel in the parachor and there is nothing unexpected about it.

Table III shows the difference between the observed and calculated values of V_0 for the associated compounds. The calculations have been made on the basis that association, as determined by the Eötvos-Ramsay method is correct and that the constant corresponding to a co-ordinate linkage with simultaneus increase in co-valency of hydrogen is 6·6.

TABLE III.

Substance	Mol. formula	Degree of association	$V_{0(obs.)}$	$V_{0(calc)}$	% Diff.
Methyl alcohol	CH_4O	3·6 (4 approx.)	149·6	152·6	+ 2·0
Ethyl alcohol	C_2H_6O	3	164·7	163·8	− 0·6
n-Propyl alcohol	C_3H_8O	2·1 (2 approx.)	143·4	141·0	− 1·7
Acetic acid	$C_2H_4O_2$	2	107·0	108·6	+ 1·5

The data were taken from the Tables Annuelles, Vol. XI (1931-34), Landolt Börnstein Tabellen and the International Critical Tables.

9

PECHMANN CONDENSATION OF *P*-ORSELLINIC ACID WITH ETHYL ACETOACETATE. · SYNTHESIS OF 7-HYDROXY-4:5-DIMETHYLCOUMARIN.

By S. M. Sethna and R. C. Shah.

· *p*-Orsellinic acid has been condensed with ethyl acetoacetate in presence of concentrated sulphuric acid yielding 7-hydroxy-4 :5-dimethylcoumarin-8-carboxylic acid. This on decarboxylation gives 7-hydroxy-4 :5-dimethylcoumarin which cannot be obtained by the Pechmann condensation of orcinol with ethyl acetoacetate. The decarboxylated product has been assigned the coumarin structure because of its non-identity with 7-hydroxy-2 :5-dimethylchromone.

Pechmann condensation of orcinol with malic acid gives 7-hydroxy-5-methylcoumarin (Pechmann and Welsh, *Ber.*, 1884, **17**, 1649), but with ethyl acetoacetate the reaction proceeds abnormally giving 5-hydroxy-4:7-dimethylcoumarin (Collie and Chrystall, *J. Chem. Soc.*, 1907, **91**, 1804). The condensation of β-resorcylic acid with ethyl acetoacetate in presence of concentrated sulphuric acid yielding 7-hydroxycoumarin derivative (Shah, *et al, J. Indian Chem. Soc.*, 1937, **14**, 717) suggested a possible method for the synthesis of the hitherto - unknown 7-hydroxy-4:5-dimethylcoumarin by the Pechmann condensation of *p*-orsellinic acid with ethyl acetoacetate and subsequent decarboxylation of the product formed.

p-Orsellinic acid condenses smoothly with ethyl acetoacetate in presence of sulphuric acid to give 7-hydroxy-4:5-dimethylcoumarin-8-carboxylic acid (I), which on decarboxylation gives 7-hydroxy-4:5-dimethylcoumarin (II).

The decarboxylated product has been characterised by the preparation of its acetyl and benzoyl derivatives and its methyl ether. It does not give, however, a cinnamic acid derivative and on heating with alkali gives orcacetophenone. These facts led the authors first to suspect that the product must be a chromone, *viz.*, 7-hydroxy-2:5-dimethylchromone, which also may be formed, as the formation of a hydroxy-ketone · on hydrolysis is believed to be the criterion of a chromone (Baker, *J. Chem. Soc.*, 1925, 2349).

The decarboxylated product has been found to be different from 7-hydroxy-2:5-dimethylchromone (III), obtained by the Claisen condensation of orcacetophenone dimethyl ether with ethyl acetate and subsequent ring-closure of the β-diketone formed. The acetyl and methoxy . derivatives of both have also been found to be different. Hence the acid has the coumarin structure (I) and the decarboxylated product is (II):

Experimental evidence has shown so far that a hydroxy-ketone is obtained only on the alkaline hydrolysis of a chromone and not a coumarin

(*cf.* Baker, *loc. cit.*), but it is quite possible that the coumarin (II) can give orcacetophenone (IV) by undergoing hydrolysis along the dotted line (*a*) after opening of the pyrone ring as shown below :—

(not isolated)　　　　(IV)

7-Hydroxy-4:5-dimethylcoumarin-8-carboxylic Acid (I).—*p*-Orsellinic acid was prepared by Robertson and Robinson's method (*J. Chem. Soc.*, 1927, 2199) by carboxylation of orcinol. On keeping *p*-orsellinic acid with ethyl acetoacetate and concentrated sulphuric acid in the cold for about 30-40 hours the condensation did not take place, *p*-orsellinic acid being recovered unchanged. On heating the above reaction mixture in a boiling water-bath for 2-4 hours, *p*-orsellinic acid was decarboxylated and the product obtained was found to be 5-hydroxy-4:7-dimethylcoumarin, which is obtained on Pechmann condensation of orcinol with ethyl acetoacetate. When, however, a temperature of 60-70° was used the condensation was quite facile

To a mixture of *p*-orsellinic acid (10 g.) and ethyl acetoacetate (8 g.), concentrated sulphuric acid (80 c.c.) was added gradually with shaking. After heating the reaction mixture for 4 hours in a-water-bath at 60-70° it was added to cold water. The product obtained was ground up with sodium bicarbonate solution and the solution on acidification gave a product which on crystallisation from rectified spirit gave tiny shining needles (4·5 g.), m. p. 225° (efferv.). It is sparingly soluble in alcohol. It gives a violet colouration with alcoholic ferric chloride and dissolves in alkali with a bluish fluorescence. (Found: C, 61·6; H, 4·5. $C_{12}H_{10}O_5$ requires C, 61·6; H, 4·3 per cent).

The portion insoluble in sodium bicarbonate. solution on crystallisation from alcohol gave pale yellow needles, m. p. 253-55°, mixed m. p. with 5-hydroxy-4:7-dimethylcoumarin prepared by Pechmann's method from orcinol and ethyl acetoacetate was the same. Pechmann and Cohen (*Ber.*, 1884, **17**, 2187) give m. p. 248°.

7-Hydroxy-4 : 5-dimethylcoumarin (II).—The above acid(2 g.) was heated in a test-tube in an oil-bath at 230-35° for 10 minutes. The acid melted with effervescence and the solid residue on crystallisation from rectified spirit gave tiny needles (1·3 g.), m. p. 248-50°. (Found : C, 68·9 ; H, 5·3. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3 per cent). Mixed m.p. with 5-hydroxy-4:7-dimethylcoumarin was depressed by about 30° and mixed m.p. with 7-hydroxy-2:5-dimethylchromone was depressed by about 40°. The product gives no colouration with alcoholic ferric chloride. It dissolves in alkali with a bluish green fluorescence.

The *acetyl derivative*, prepared as usual with pyridine and acetic anhydride, was crystallised from rectified spirit in needles, m.p. 119-21°. (Found: C, 66·6; H, 5·0. $C_{13}H_{12}O_4$ requires C, 66·7; H, 5·1 per cent).

The *benzoyl derivative*, prepared as usual with benzoyl chloride and pyridine, was crystallised from rectified spirit in shining needles, m. p. 130-31°. (Found: C, 73·2 ; H, 4·8. $C_{18}H_{14}O_4$ requires C, 73·5 ; H, 4·8 per cent).

The *methyl ether*, prepared as usual with sodium hydroxide and dimethyl sulphate, was crystallised from rectified spirit in needles, m.p. 117-19°. (Found: C, 70·5 ; H, 5·7. $C_{12}H_{12}O_3$ requires C, 70·6 ; H, 5·9 per cent).

Hydrolysis of 7-Hydroxy-4:5-dimethylcoumarin.—The coumarin (0·5 g.) was heated on a boiling water-bath with sodium hydroxide (10%; 15 c.c.) for 5 hours. The solution was acidified with hydrochloric acid and the product obtained on cooling was crystallised from aqueous alcohol in needles, m p. 157-59°. Mixed m.p. with orcacetophenone prepared by Hoesch's method (*Ber.*, 1915, **48**, 1127) was not depressed.

(2':4'-Dimethoxy-6'-methyl)-benzoylacetylmethane.—Dimethyl ether of orcacetophenone (6 g.) and ethyl acetate (11 g., approx. 4 mols) were added to pulverised sodium (1·5 g., approx. 2 mols.), the whole being cooled externally by cold water. After the initial vigorous reaction had subsided the reaction mixture was heated in an oil-bath at 115-20° for 1 hour. On cooling water was added to the reaction mixture and it was extracted with ether to remove the excess of ethyl acetate and the unreacted dimethylether of orcacetophenone. The alkaline solution was acidified with dilute acetic acid when an oil separated which soon solidified.

It crystallised from dilute alcohol in pale yellow needles (4·5 g.), m.p. 74-76°. It gives a reddish violet colouration with alcoholic ferric chloride (Found: C, 66·3 ; H, 6·9. $C_{13}H_{16}O_4$ requires C, 65·8 ; H, 7·3 per cent).

The *copper salt*, prepared from the β-diketone and copper acetate, was crystallised from benzene in tiny greenish needles, m.p. 198-200°. [Found : Cu, 11·8. $(C_{13}H_{15}O_4)_2$ Cu requires Cu, 11·9 per cent] This salt on decomposition with 10% sulphuric acid gives the original β-diketone back.

7-Methoxy-2:5-dimethylchromone.—To the above β-diketone (2 g.), dissolved in the minimum quantity of acetic anhydride, hydrobromic acid solution (d 1·78, 10 c.c) was added and the reaction mixture left overnight. The product obtained on adding the reaction mixture to water was treated with dilute sodium hydroxide solution to remove any hydroxy-chromone formed. The alkaline solution, however, gave practically nothing on acidification with hydrochloric acid. The alkali-insoluble portion crystallised from rectified spirit as needles (0·8 g.), m.p. 150-52°. (Found : C, 70 8 ; H, 5·9. $C_{12}H_{12}O_3$ requires C, 70·6 ; H, 5·9 per cent).

7-Hydroxy-2:5-dimethylchromone.—The methyl ether (0·5 g.) was dissolved in acetic anhydride (3 c.c.) and hydriodic acid (d 1·7, 5 c c.) added gradually. The reaction mixture was refluxed in an oil-bath at 130-40° for 2 hours and then added to sodium bisulphite solution. The product which separated was treated with sodium hydroxide (5 %, 15 c c.). The small quantity of the insoluble portion was found to be the undemethylated methyl ether described above. The alkaline solution was acidified and the product obtained crystallised from rectified spirit in pale yellow glistening needles (0·3 g.), m.p. 253-55°. (Found : C, 69·7 ; H, 5·3. $C_{11}H_{10}O_3$ requires C, 69·5 ; H, 5·3 per cent). The product dissolved in sodium hydroxide and in concentrated sulphuric acid with greenish flourescence.

The *acetyl derivative*, prepared as usual with sodium acetate and acetic anhydride, crystallised from rectified spirit in long woolly needles, m.p. 195-97°. (Found : C, 67·3 ; H, 5·2. $C_{13}H_{12}O_4$ requires C, 66·7 ; H, 5·1 per cent).

The styryl derivative could not be obtained either from hydroxy-chromone or its methyl ether and piperonal.

Attempts to hydrolyse the chromone methyl ether by refluxing it with 50% alcoholic caustic potash for 16 hours gave the methyl ether back.

EXTENSION OF REFORMATSKY REACTION. PART I. STUDY WITH ETHYL BROMOMALONATE AND ACETONE.

By BALKRISHNA H. IYER.

Reformatsky reaction with ethyl bromomalonate and acetone follows an unexpected course. One molecule of the former reacts with two molecules of the latter leading to the formation of ethyl acetonyl*iso*propylmalonate which has been characterised by its cyclisation to 5:5-dimethyldihydroresorcin and hydrolysis to a dilactone. The mechanism of the reaction is explained.

The classical Reformatsky reaction for the synthesis of β-hydroxy-esters consists in the condensation of the α-bromo-ester of a monocarboxylic acid with a ketone in the presence of zinc. Studies with various ketones and oxides, and α-chloro-, bromo- or iodo- esters of monocarboxylic acids are reported in literature (Lawrence, *J. Chem. Soc.*, 1897, 71, 457 ; Clemo and Ormston, *ibid.*, 1933, 362 ; Johnson, *J. Amer. Chem. Soc.*, 1913, 35, 582; Nieuwland and Daly, *ibid.*, 1931, 53, 1842 ; Fuson and Farlow, *ibid.*, 1934, 56, 1593 ; Myers and Lindwall, *ibid.*, 1938, 60, 644 ; Fuson *et al.*, *ibid.*, 1938, 60, 2272 ; Arbusow, *Ber.*, 1935, 68, 1430). Having failed to see any mention of a Reformatsky's synthesis using the α-halogen ester of a dibasic acid, it was thought to be of interest to study the reaction of ethyl bromomalonate with acetone in the presence of zinc. (*Proc. Indian Science Congress*, 1935, p. 146). Under the normal course the β-hydroxy-ester (I) would be expected.

$$Me_2C(OH)\cdot CH(CO_2Et)_2 \quad (I)$$

But the reaction takes a different course leading to the formation of acetonyl*iso*propylmalonate (II) (b. p. 135-137°/4 mm.) from two molecules of acetone and one molecule of ethyl bromomalonate. The structure of (II) was proved by its cyclisation to 5:5-dimethyldihydroresorcin (III) (semicarbazone, m.p. 74-75° ; Vorlander and Erig, *Annalen*, 1897, 294, 314) on treatment with sodium methylate and subsequent hydrolysis with alkali. On hydrolysis with hydrochloric acid the ester (II) gives the dilactone (IV) (m.p. 135-36°). Qudrat-i-Khuda (*J. Chem. Soc.*, 1929, 204) prepared (II), which he named as ethyl ester of α-carboxy-γ-acetyl-$\beta\beta$-dimethylbutyric acid and the dilactone (IV) by the condensation of mesityl oxide with cyanoacetamide. The alkali hydrolysis of 6-hydroxy-2-keto-3-cyano-4:4:6-trimethylpiperidine (V) gave the acid (VI) which

was esterified to (II) and subsequently cyclised to (III). When the piperidine derivative (V) was hydrolysed with hydrochloric acid the dilactone (IV) was formed. The melting points of the products (IV) and the semicarbazone showed no depression when admixed with the respective ones prepared according to Qudrat-i-Khuda.

Iyer　　　　　　　　　　　　　Qudrat-i-Khuda

$Me_2CO + CHBr(CO_2Et)_2$　　　　　　$Me_2C=CH \cdot CO \cdot Me$
$+$
$CN \ CH_2 \cdot CO \cdot NH_2$

(II)　　　　　　　(V)

(III)　　　　　　(IV)　　　　　(III)

In all the experiments excess of acetone (3 molecules to one of bromo-ester) was used. Suspecting that the excess of the ketone was misdirecting the normal Reformatsky reaction, in a trial experiment only molecular proportions were used. However, the product isolated was the same (II) ; only a quantity of zinc and ethyl bromomalonate were recovered unreacted, thus indicating the need for excess of acetone. Further from the low boiling fractions of the reaction mixture, mesityl oxide was isolated. Therefore, it becomes necessary to assume that due to the influence of zinc and ethyl bromomalonate, formation of mesityl oxide takes place in the system. Kohler, Heritage and Macleod (*Amer. Chem. J.*, 1911, **46**, 217) have studied the action of methyl bromomalonate on benzalacetophenone in presence

of zinc, where due to 1:4-addition at the conjugated system, methyl-γ-benzoyl-β-phenylethylmalonate (VII) is formed as under

$$Ph \cdot CH = CH \cdot CO \cdot C_6H_5 + CHBr\,(CO_2Me)_2 +$$

$$\overset{Zn}{\downarrow}$$

$$Ph.CH - CH = C(OZnBr)Ph$$
$$\underset{CH(CO_2Me)_2}{|}$$

$$Ph \cdot CH - CH = C(OH) \cdot Ph \qquad \rightarrow \qquad Ph \cdot CH - CH_2 - CO \cdot Ph$$
$$\underset{CH(CO_2Me)_2}{|} \qquad\qquad\qquad \underset{CH(CO_2Me)_2}{|}$$

$$(VII)$$

They have established that with bromomalonic esters and unsaturated ketones only 1:4-addition happens under these conditions. In analogy to this, the mechanism of the present reaction is explained as follows. Two molecules of acetone condense to give mesityl oxide. Later the zinc compound of ethyl bromomalonate adds on to it in 1:4-position leading to the formation of (II) as below.

$$Me_2C = CH \cdot CO \cdot Me + CHBr(CO_2Et)_2 \overset{Zn}{\longrightarrow} Me_2C - CH = C(OZnBr)Me$$
$$\underset{CH(CO_2Et)_2}{|} \longrightarrow$$

$$Me_2C - CH = C(OH)Me \qquad \rightarrow \qquad Me_2C - CH_2 - CO \cdot Me$$
$$\underset{CH(CO_2Et)_2}{|} \qquad\qquad\qquad \underset{CH(CO_2Et)_2}{|}$$

$$(II)$$

Apparently this is not a true Reformatsky reaction although molecular proportion of zinc is consumed. The possibility of the formation of the hydroxy-ester (I) in the early stages of the reaction and its subsquent condensation with another molecule of acetone to form (II) is ruled out as there is neither any indication during the present investigation nor any mention of a parallel case in literature. Incidentally, experiments using diacetone alcohol and mesityl oxide instead of acetone, also yield only (II).

It is hoped to extend the work with other ketones and halogen esters of dibasic acids.

Experimental.

Ethyl bromomalonate was prepared by brominating malonic ester in carbon tetrachloride (Organic Synthesis, 1927, VII, 34).

Ethyl Acetonylisopropylmalonate (II).—To ethyl bromomalonate (47·8 g.) and dry acetone (34·8 g.) taken in a 500 c.c. round bottomed flask fitted with a reflux condenser and guard tube, and heated on a water-bath purified zinc wool (14 g.) was added in small quantities. Very often the reaction commenced immediately ; on occasions it had to be started by the addition of a trace of iodine. After the entire zinc was added it was refluxed for about 2 hours and the excess of acetone distilled off. Water was then added and the resulting mixture was treated with dilute sulphuric acid. The separated oil was taken up in ether, the ethereal solution was successively washed with dilute sulphuric acid and water, and finally dried with magnesium sulphate. The residual oil (23 g.) from ether was distilled at 170-175°/34-36 mm., or at 135-37°/4 mm., yield 9 g. (Found : C, 60·31 ; H, 8·53. M. W., 256 9. $C_{13}H_{22}O_5$ requires C, 60·47 ; H, 8·53 per cent. M.W., 258).

Cyclisation of (II) *to* 5:5-*Dimethyldihydroresorcin* (III).—Ethyl acetonyl*iso*propylmalonate (12 g.) was cyclised by refluxing it for $2\frac{1}{2}$ hours with anhydrous methyl alcohol (50 c.c.) in which sodium (1·5 g.) was dissolved. The mixture was again refluxed for another 5 hours after the addition of caustic potash solution (8 g. in 100 c.c. of water). Alcohol was then removed and the product isolated after acidification with hydrochloric acid, m.p. 146-48° (mixed m.p. with a genuine sample), yield 3 g.

The semicarbazone, prepared in the usual manner, crystallised from ethyl alcohol, m.p. 74-75° (mixed m.p. with Qudrat-i-Khuda's preparation), yield 3 g. (Found : N, 13·06. Calc. for $C_{14}H_{25}O_5N_3$: N, 13·33 per cent).

Hydrolysis of (II) *and Formation of the Dilactone* (IV).—The ester (II, 5 g.) was refluxed with dilute hydrochloric acid (1.1, 40 c.c.) till the oily layer disappeared. It was then filtered and evaporated to dryness. The pasty mass was purified by successive treatment with acetone and benzene and the solid crystallised from water, m.p. 135-36°, yield 1 g. (mixed m.p. with Qudrat-i-Khuda's product). (Found : C, 58·98 ; H, 6·49. Calc. for $C_9H_{12}O_4$: C, 58·73 ; H, 6·52 per cent).

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KINETICS OF .THE REACTION BETWEEN POTASSIUM PERSULPHATE AND THE ALKYL IODIDES. PART II.

By M. S. Telang and V. V. Nadkarny.

The rate of the persulphate-alkyl iodide reaction increases with dilution and the calculated velocities are in good agreement with the observed values. The relative chemical reactivities of the alkyl iodides in the homologous series have been determined and the results are analysed on the basis of the equation $k = PZe^{-E/RT}$. P is found to be less than unity and there is a simultaneous decrease of activation energy and the probability factor in passing from methyl to n-butyl iodide. The secondary, tertiary and *iso*alkyl iodides are more reactive than the corresponding primary compounds.

Hecht, Conrad and Brückner (Z. physikal. Chem., 1890, 5, 289) found that the velocity of the methyl iodide - sodium ethoxide reaction varied with the dilution as $k_v = k_1 + \omega \log_{10} v$. Cox (J. Chem. Soc., 1918, 113, 666; 1921, 119, 143; 1922, 121, 1904) observed this equation to be applicable to a similar series of reactions. Kappanna has indicated in the decarboxylation of trichloracetic acid in water (Z. physikal. Chem., 1932, A, 158, 355) that the effect of dilution is no greater than with bimolecular reactions. These investigations are of value since at great dilutions the observed rates and those calculated from the Arrhenius equation are brought into closer agreement, as observed in a large number of reactions (Moelwyn-Hughes, " Kinetics of Reactions in Solutions", 1933, p. 79). Attempts had therefore to be made to determine the suitable dilution for comparable results.

Owing to the increasing importance of the alkyl halides in synthetic and preparative organic chemistry, various attempts have been made to study their chemical reactivities with a variety of reagents. Consequently, numerous papers on the subject have been published, (Brussof, Z. physikal. Chem., 1900, 34, 129; Menschutkin and Wassilieff, ibid., 1890, 5, 539, Wislicenus, Annalen, 1882, 212, 244 ; Segaller, J. Chem. Soc., 1914, 105, 106; Burke and Donnan, ibid., 1904, 85, 555; Haywood, ibid., 1922, 121, 1904; Preston and Jones, ibid., 1912, 101, 1930 ; Slator, ibid., 1904, 85, 1286 and others). Most of these reactions are considered to be metathetical. Therefore, a study of the relative chemical reactivities of alkyl iodides with an oxidising agent like potassium persulphate would be of special interest. Further, this part of work was undertaken to determine the effect of

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" weighting " the alkyl iodide molecule in this reaction with CH_2 groups, on the parameters of the Arrhenius equation $k = PZe^{-E/RT}$.

EXPERIMENTAL.

The analytical procedure has been described -in a previous paper (Telang and Nadkarny, *J. Indian Chem. Soc.*, 1939, **16**, 536).

Effect-of Dilution.—0·2 N-Alcoholic solution (10 c.c.) of C_2H_5I and 0·2 N-solution (10 c.c.) of $K_2S_2O_8$. were mixed together and then made up to the required total volume with water. The reaction mixture was heated in the thermostat for two hours in each case at 50°. The effect of dilution was also studied with 50% alcohol (effective composition of the solvent) in place of water as the diluent. Table I contains both the sets of observations.

TABLE I.

$\omega = 110·8 \times 10^{-6}$. $k = 42·7 \times 10^{-6}$

Dilution (v) (litre/g.-mol.)	Velocity constant $k \times 10^6$ (with 50% alcohol).	Velocity constant (with water).	
		$k \times 10^6$ (obs.)	$k \times 10^6$ (calc.)
10	147·7	153·5	154.0
20	143·9	174·6	186·8
40	78·7	228·2	220·1
80	30·7	254·1	253·5
160	—	272·3	286·8

The Relative Chemical Reactivities of the Alkyl Iodides.—The alkyl iodides were prepared from their corresponding alcohols by the standard method, the alcoholic group being replaced by iodine in presence of red phosphorus. For the determination of the velocities of the different iodides, 0·2N alcoholic solution (10 c.c) of alkyl iodide and 0·2N solution of $K_2S_2O_8$ (10 c.c.) were made up to 100 c.c. with water (dilution $v = 50$) and heated for two hours .at the required temperature. The results are shown in Table II.

The collision frequencies Z have been calculated from the equation (Moelwyn-Hughes, *J. Chem. Soc.*, 1932, 95)

$$Z = 3\pi N \eta \sigma_A / 2M_A \times (M_A + M_s)/M_s,$$

where M_s is the molecular weight of the solvent (water), M_A that of the alkyl iodide and other terms have their usual significance. As the effective

composition of the solvent is only 10% alcohol, M_s is taken as the mol. wt. of water. The Arrhenius energy of activation has been corrected for the viscosity factor, Rb in the relation $E = E_A + Rb$ (cf. Andrade, *Nature*, 1930, **125**, 309). Within the range of 50° and 60° the temperature coefficients of the viscosity of alcohol and water are not very different so that the values of water are used for correcting the Arrhenius energy of activation. This effect in all cases is to increase E_A by 3,425 calories. So the theoretical velocities given below are corrected for this viscosity factor. As the Arrhenius equation is not accurately obeyed (*vide*, Telang, Thesis, Bombay University, 1939) the critical increments have been calculated from the values of the velocity constants at two temperatures only, *viz.* 50° and 60°.

TABLE II.

Alkyl iodide.	Relative chemical reactivity at 50° ($C_2H_5I=100$).	Temp. coeff. $k_{60}°/k_{50}°$.	$k_{50}°$ (min.$^{-1}$) (obs.)	$k_{50}°$ (min.$^{-1}$) (calc.)	E_A (calories).	Collision frequency. Z (sec.$^{-1}$)	$P = \dfrac{k \text{ obs.}}{k \text{ calc.}}$.
Mehyl	60	2·57	115×10^{-6}	444×10^{-3}	20,120	$6·6 \times 10^{13}$	$0·26 \times 10^{-2}$
Ethyl	100	2·51	192	989 ,,	19,650	7·0	$0·20 \times 10^{-?}$
n-Propyl	54	2·09	104	456	15,760	7·5	$0·23 \times 10^{-6}$
n-Butyl	8	2·00	15	$212 \times 10^{+1}$	14,800	7·7	$0·20 \times 10^{-7}$
*iso*Propyl	356	2·87	683	906×10^{-6}	22,500	7·6	0·75
*tert*Butyl	68	4·27	130	244×10^{-10}	30,970	8·1	$0·53 \times 10^{+4}$

The relative chemical reactivities of *iso*butyl, *sec*-butyl, *n*-amyl and *iso*amyl are 151, 19, 13 and 35 respectively.

DISCUSSION.

The velocity of the persulphate-alkyl iodide reaction increases with dilution up to at least $v = 160$, and the velocity at a dilution $v = 160$ is about six times faster than (k_1) calculated for unit molar concentration. From a graphical representation of the dilution effect, it is evident that the most suitable dilution required for comparable results is $v = 50$, as this dilution is sufficiently great without causing much inconvenience regarding the bulk of the reaction mixture to be handled. Examining the values of the velocities with water as well as 50% alcohol it is obvious that the presence of alcohol retards the reaction rate

whereas water accelerates it. We do not yet attempt to explain the mechanism of the dilution effect.

Since the probability factor P, for the normal alkyl iodides is less than unity, the reaction is classed as a " slow " unimolecular reaction. A close examination of Table II reveals that the P factor decreases as the critical alkyl iodide increment E_A decreases. This concurrence shows that the slowness of the persulphate-alkyl iodide reaction is to be ascribed exclusively to the increase of the energy of activation necessary for the oxidation of the alkyl iodides by potassium persulphate. These results are analogous to those in some cases of quaternary salt formation (Winkler and Hinshelwood, *J. Chem. Soc.*, 1935, 1147). The change from methyl to ethyl results in no alteration in P, but there is a marked fall in P from methyl to n-propyl iodide; further, the change from n-propyl to n-butyl produces a slight alteration in P. These observations are in fair agreement with the general hypothesis that in a series of straight-chain compounds, beyond the 3rd or 4th addition of CH_2 group, the effect on P is relatively unimportant. Yet, the variation in the Arrhenius activation energy is observed to decrease by about 5000 calories in passing from methyl to n-butyl iodide.

The order of relative chemical reactivities of alkyl iodides in this reaction runs almost parallel with that in the reaction with silver nitrate (Burke and Donnan, *loc. cit.*). Further, these data show the greater tendency of the cleavage of iodine from secondary compounds and still more from tertiary compounds , *iso*-compounds, however, are the most reactive. The differences between the primary and secondary compounds may be real or they may be due to a different mechanism being operative (*cf.* Conant, Kirner and Hussey, *J. Amer. Chem. Soc.*, 1924, **46**, 232; 1925, **47**, 476, 488).

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BIOLOGICAL VALUE OF THE PROTEINS OF BENGAL FISH

By K. C. Saha.

The biological values of three different varieties of fish, which are commonly consumed, namely, *chingri*, *singhi* (*Saccobranchus fossilis*) and *Air* (*Arius arius*) have been investigated by the growth method. From the results it appears that the biological values of *chingri*, *shinghi* and *air* at 5 and 10% levels are superior to that of casein. Compared among themselves, *air* is superior to both *chingri* and *shinghi* at 5% levels, while at 10% levels they are all approximately equivalent.

As fish constitutes an important article in the daily diet in Bengal, it is desirable to determine the biological value of the proteins of the different varieties of fish, which are commonly consumed. In the present communication investigations of the three varieties, *viz.*, *chingri*, *singhi* (*Saccobranchus fossilis*), and *air* (*Arius arius*) are reported. The biological values of the proteins of these fish were determined by the growth of young rats. When this work was ready for the press, a paper was published by Basu and Gupta (*J. Indian Chem. Soc.*, 1939, **16**, 543), in which figures for the biological value of *shinghi* and *air* proteins were given. Their results are discussed later.

Experimental.

Prior to the biological assay, the fish samples were analysed with reference to their moisture, total nitrogen, ash and fat contents by the methods described by Saha and Guha (*Indian J. Med. Res.*, 1939, **26**, 921).

Table I.

Percentage composition of the fish used as sources of protein.

Bengali name.	Zoological name.	Moisture.	Fat.	Total nitrogen.	Protein.	Ash.
Chingri	—	73	1·6	3	18·8	4·1
Singhi	*Saccobranchus fossilis*	68	0·6	3·6	22·8	2·7
Air	*Arius arius*	78·1	1·3	2·5	15·9	1·15

The tests were carried out with young albino rats in separate cages with screened bottoms essentially by the method used by Boas-Fixsen,

TABLE II.

Biological value of proteins of fish and of casein by the growth method.

Materials.	Protein in diet.	No. of rats.	Period of expt.	Increase in weight		Total food intake		Protein intake (mean).	B.V
				Variation.	Mean.	Variation.	Mean.		
Chingri fish	5 %	4	5 week.	7-22	16	122-174	151 5	8·42	1·90
	10	4	5	22-52	35·25	157-175	169·5	17·45	2·00
	15	4	5	33-48	40·75	164-208	191·5	29 49	1·38
Singhi fish	5	4	5	16-19	17·25	146-187	161·5	8·35	2·09
	10	4	5	38-45	41·25	187-213	203·25	19·91	2·07
	15	4	5	61-72	64·75	190-232	215·0	32·07	2·02
Air fish	5	3	5	12-15	13·67	126-139	131·0	6·11	2·27
	10	4	5	31-40	37·25	185-212	199·5	19·20	1·94
	15	4	5	44-54	51·5	191-230	216·5	33·01	1·56
Casein	10	4	5	23-34	28·5	169-171	170·0	17·2	1 67
	15	4	5	46-51	48·5	192-194	193·0	20·31	1 66

At 5 % casein level the rats did not show any appreciable growth; so the results were discarded being of no significant value.

B.V. = gain in weight./protein intake.

Hutchinson and Jackson (*Biochem. J.*, 1934, **28**, 592) and by Basu, Nath and Ghani (*Indian J. Med. Res.*, 1936, **23**, 811). Each diet consisted of cane sugar (7·5 %), olive oil (12·0 %), cod-liver oil (2·0 %), Steenbock's salt mixture (No. 40) (4·0 %) and calcium carbonate (1·0 %). The fish meal (prepared by mincing, drying at 40.° and powdering) was incorporated at such levels in the diets on the basis of their analytical figures (Table I) that they constituted protein levels of 5, 10 and 15 % of the diets. The differences in the fish meal levels were made up by proportionately altering the starch contents of the diets. Four rats were kept on each diet. 0·5 G. of yeast was fed to each rat once a week as a source of vitamin B-complex. It supplied a negligible fraction of the total nitrogen and hence was not taken into account. The actual experimental period for which records were taken began from the 2nd week and lasted for 5 weeks. The biological values were then calculated from the ratio of the total protein intake to the total gain in body weight in five weeks. For comparison, two rats were kept on normal diet consisting of whole wheat and milk, supplemented occasionally by cod-liver oil, and six rats were kept on a synthetic diet containing 5, 10 and 15 % of casein. The data on growth, protein-intake and biological values with different fish meals are summarised in Table II.

DISCUSSION.

The mean biological values of chingri, air, singhi and casein at 5, 10 and 15% protein levels are summarised in Table III.

TABLE III.

Biological values.

Protein.	At 5% level.	At 10% level.	At 15% level.
Air	2·27	1·94	1·56
Singhi	2·09	2·07	2·02
Chingri	1·90	2·00	1·38
Casein	—	1·67	1·66

From the above table, it is clear that the biological values of *chingri, singhi* and *air* at 5 and 10% protein levels are superior to that of casein. Compared among themselves, *air* is superior to both *chingri* and *shinghi* at 5% levels, while at 10% levels they are all approximately equivalent. With 5%

casein diet, the rats did not show any appreciable growth. Taking growth as the criterion of biological value of a protein, casein appears, therefore, to be inferior to the proteins of *chingri, singhi* and *air* at 5% protein levels.

As the proportion of protein goes up in the diet, however, the biological values approximate to one another. On the whole, all these fish proteins are high-class proteins, *singhi* having the highest biological value at 10 and 15% protein levels. In the paper of Basu and Gupta (*loc. cit.*) concerning the biological values of the proteins of some species of fish, the authors gave the values 1·97 and 1·84 for *air* and *singhi* respectively at 15% protein levels in the diet. In our experiments they are respectively 1·56 and 2·02. The differences may be due to differences in season or source or variety, but all the figures indicate first-class proteins.

With all the sources of protein under investigation, except *chingri*, it is found that the biological value decreases as the concentration of protein in the diet increases. But it is interesting to note that in the case of *chingri*, the biological value at first increases from 1·9 to 2·00 as the percentage of protein in the diet increases from 5 to 10 and then the value decreases from 2·00 to 1·38 as the concentration of protein increases from 10 to 15%. Osborne, Mendel and Ferry (*J. Biol. Chem.*, 1919, **37**, 223) record observations showing that the biological value may reach a maximum at a certain protein level and then decline. The *chingri*, however, is not a fish and may conceivably differ in the above respect from the fishes investigated. The subject, however, deserves further study.

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CHEMOTHERAPY OF BACTERIAL INFECTIONS. PART I. SUBSTANCES RELATED TO SULPHANILAMIDE. SYNTHESIS OF P-AMINOBENZYLSULPHONAMIDE AND ITS DERIVATIVES

BY P. L. NARASIMHA RAO.

p-Aminobenzylsulphonamide and its derivatives have been prepared for pharmaco-logical study with a view to throwing further light on the relation between chemical constitution and antistreptococcal action as well as the mechanism of chemothera-peutic action of sulphanilamide drugs.

The specific antistreptococcal action of the red-dye, prontosil (hydrochloride of 4-sulphamido-2':4'-diaminoazobenzene (I, R=H), (Domagk, *Deut. Med. Wschr.*, 1935, **61**, 250; *Z. angew. Chem.*, 1935, **48**, 657; *Klin. Wschr.*, 1936, **15**, 1585), and the striking therapeutic effect of the previously known simpler compound, sulphanilamide, (II, R=R'=H) and

many of its derivatives of the type R·NH⟨ ⟩SO$_2$R' in various bac-

(I)   (II)

terial infections have stimulated widespread interest and renewed activity in chemotherapy of infectious disease. Thus there have come into medical practice a host of sulphanilamide derivative like prontosil sol (III), rubiazol (I, R=CO$_2$Na), septazine (II, R= C$_6$H$_5$CH$_2$; R'=H), soluseptazine (IV) for use in cases of erysipelas, strept. angina, puerpeural sepsis, strept. meningitis, etc. Apart from these,

(III)

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$$\langle\ \rangle-CH-CH_2-CH-NH\langle\ \rangle SO_2NH_2$$
$$\qquad\quad |\qquad\qquad\quad |$$
$$\qquad\quad SO_3Na\qquad SO_3Na$$

(IV)

sulphanilamide drugs have also been used with success in the treatment of coli infections of genito-urinary tract (due to *B. coli* and *Proteus ammoniae*) and in that of pneumococcus and meningoccus infections. Some sulphanilamide derivatives containing substituted residues in the sulphonamide group are shown to be active in the staphylococcal, anærobic and above all in gonococcal infections. Of these compounds uleron (Baeyer), 4-(4′-amino-benzene)- sulphonamidobenzenesulphonyi

dimethylamine (II, R=H; R′= $-\langle\ \rangle SO_2NMe_2$) and albucid (Schering)

(II, R=H ; R′=COMe) find favour in the treatment of gonorrhoea.

$$H_2N\langle\ \rangle SO_2NH\langle^{N-}_{\ }\ \rangle$$

$$NH_2$$
$$\bigcirc$$
$$(CH_2)_n\cdot SO_2NH_2.$$

(V)   (VI)

Perhaps the greatest achievement in this line lies in the discovery of sulpha-pyridine (V) (M. and B. 693 ; Dagenan) for the treatment of pneumococcal-pneumonia and to lesser extent also meningitis staphylococcal septicemia, chronic meningococcal septicemia, subacute bacterial endocarditis and also pempligus.

It is clear from the foregoing that researches in this branch of chemotherapy are progressing on two main lines namely towards the preparation of (i) drugs more effective and less toxic than sulphanilamide, and (ii) drugs effective in bacterial and virus infections in which sulphanilamide and its derivatives fail.

This investigation has been undertaken with the object of following the course of the above two lines. Firstly it is intended to prepare new type of compounds but closely related to sulphanilamide and test their therapeutic action against bacterial infections especially against those not responding favourably with known drugs. It is also proposed to prepare some new derivatives of sulphanilamide likely to possess antibacterial activity.

Till now most of the drugs employed for the treatment of bacterial infections contain sulphur and all the recent drugs of sulphanilamide group possess sulphur residues directly attached to the benzene nucleus. However, Buttle and his collaborators (*Biochem. J.*, 1938, **32**, 1101; *cf.* Marshall, *Physiol. Rev.*, 1939, **19**, 240) state that 4:4'-dinitrodiphenylmethane, 4:4'-dinitrodiphenyl oxide, and 2:2'-dinitro-4: 4'-diaminodiphenylmethane possess some activity and Bittenbunder and Degaring (*J. Amer. Pharm. Assoc.*, 1939, **28**, 515) recently report bacteriostatic effect of *para*-substituted phenyl. acetic acid derivatives on staphylococcus aureus and E. coli in *vitro*. In the light of these observations it was thought of interest, in the first place, to ascertain what bactericidal activity the compounds of the type (VI) having an aliphatic side-chain between the benzene nucleus and the sulphamido group possess and so *p*-aminobenzyl sulphonamide and some of its derivatives have now been prepared.

Marshall (*loc. cit.*) states " little or no activity is found in mononuclear compounds in which.........the sulphonamide group (is replaced) by groups *not yielding a sulphonic acid on oxidation*." This statement may be of special significance since it is becoming known that oxidation products of sulphanilamide (Shaffer, *Science*, 1939, **89**, 547) are the real therapeutic agents *in vivo*. Hence it is evidently desirable to ascertain how the greater facility of oxidation of the sulphonamide group in *p*-aminobenzylsulphanilamide as compared to that in sulphanilamide, augments the activity of the latter. It is with this object in view a study of the oxidation potential of *p*-aminobenzylsulphonamide under conditions similar to those employed for sulphanilamide, is being actively pursued. The results of physico-chemical and the pharmacological experiments will be published in due course.

EXPERIMENTAL.

Sodium p-*nitrobenzylsulphonate* was conveniently prepared by the following modification of the method outlined in D. R. P., 55,138 (*Frdl.*, **II**, 386; *cf.* Purgotti, Monti and Designs, *Gazzetta*, 1900, **30**, 247; Ingold *et al.*, *J. Chem. Soc.*, 1927, 813).

A mixture of *p*-nitrobenzyl bromide (21·6 g.; chloride, 17·2 g.), anhydrous sodium sulphite (12·6 g.), water (100 c.c.) and alcohol (300 c.c.) was boiled under reflux till a fairly clear solution was obtained (6 hours). Alcohol was then removed by distillation and the solution after filtering

from a little tar, was concentrated to about 50 c.c. The sodium salt of the sulphonic acid that crystallised out was separated and recrystallised from alcohol, yield 20 g.

p-*Nitrobenzylsulphonyl Chloride and Amide.*—The acid chloride (Ingold, *loc. cit*) was purified by crystallisation from benzene-ligroin mixture. The amide (Mohr, *Annalen*, 1883 **221**, 218) was conveniently crystallised from dilute pyridine.

p-*Aminobenzylsulphonamide* was obtained by the reduction of the above nitrosulphonamide with ammonium sulphide or tin and hydrocloric acid. In the first method a mixture of the nitro compound (10 g.), alcohol (100 c.c.), water (50 c.c.) and liquor ammonia (30 c.c.) was saturated with hydrogen sulphide and then gently boiled for 1 hour under reflux. This procedure was repeated thrice adding more liquid ammonia, till the whole nitro compound went into solution. The product was then boiled with a little more water for a few minutes and concentrated after neutralisation with hydrochloric acid and filtration of the precipitated sulphur. On making the solution ammoniacal, the amino compound, m.p. 168°, separated in pale yellow powder which was recrystallised from hot water (charcoal) to which a few drops of ammonia were added to remove the persistent yellow colour, yield 5·4 g. (Found: N, 15·1; S, 17·2. $C_7H_{10}O_2N_2S$ requires N, 15·05; S, 17·20 per cent).

Reduction of the nitro compound with tin and hydrochloric acid in the usual way proceeded more smoothly and the yield of the amino compound was invariably better. It is easily soluble in hot water and pyridine, fairly in alcohol and difficultly in other usual organic solvents. Its solutions in dilute acids are pale yellow and its diazotised solution coupled easily with β-naphthol.

The amine rapidly turns yellow on exposure to air and its solutions often acquire a characteristic pinkish yellow colour on standing exposed to air and light. This is perhaps significant in the light of the statements of Shaffer about the oxidation products of sulphanilamide.

The *acetyl derivative* crystallised from hot water in colourless stout prism-like crystals, m.p. 212°. (Found : N, 12·2. $C_9H_{12}O_3N_2S$ requires N, 12·32 per cent). The *valeryl derivative* was obtained as colourless leaflets, m.p. 188-89°. (Found : N, 10·5. $C_{12}H_{18}O_3N_2S$ requires N, 10·33 per cent) and the *caproyl derivative* as silvery-white plates, m.p. 192-94°. (Found : N, 9.9. $C_{13}H_{20}O_3N_2S$ requires N, 9·86 per cent). They were both prepared

by the action of the respective acid chloride on the amine in pyridine solution and crystallising the products from dilute alcohol.

The *benzoyl derivative*, prepared in a similar manner, was sparingly soluble in many of the usual solvents and crystallised from alcohol in microscopic crystals, m.p. 230-31°. (Found : N, 9·5. $C_{14}H_{14}O_3N_2S$ requires N. 9·66 per cent).

The following derivatives substituted at the amino group of the above compound were prepared by condensing together equimolecular quantities of *p*-nitrobenzylsulphonamide and the appropriate amine in benzene solution in presence of pyridine, and the resulting nitro compounds were then reduced.

p-*Nitrobenzylsulphanilide* crystallised from pyridine, m.p. 130-31°. (Found : N, 9·8. $C_{13}H_{12}O_4N_2S$ requires N, 9·59 per cent).

p-*Aminobenzylsulphanilide.*—To a mixture of the above nitro compound (5 g.), granulated tin (10 g.), hydrochloric acid (20%, 30 c.c.) was added gradually with shaking and the product heated on a water-bath till the nitro compound went into solution. It was then diluted, filtered and freed from tin by precipitating it as tin sulphide. The concentrated filtrate deposited colourless feathery needles, the hydrochloride of p-*aminobenzyl-sulphonanilide* melting at 168-70° (decomp.). (Found : N, 9·4. $C_{13}H_{14}O_2N_2S$. HCl requires N, 9·05 per cent). The hydrochloride was dissolved in water and made just ammoniacal whereupon the free base separated out. It was recrystallised from water in colourless plates, m.p. 172-73°. (Found : N, 10·7. $C_{13}H_{14}O_2N_2S$ requires N, 10·73 per cent).

p-*Nitrobenzylsulphonyl-2-aminopyridine.*—p Nitrobenzylsulphonyl chloride (4·8 g.) in benzene (20 c.c.) was gradually added under shaking to a solution of 2-aminopyridine (4·5 g.) in benzene (20 c.c.). The separated solid was filtered, washed with a little water and benzene and crystallised from pyridine. The nitro compound separated in colourless stout prisms, m.p. 214-15°, sparingly soluble in many of the ordinary solvents. (Found : N, 14·3. $C_{12}H_{11}O_4N_3S$ requires N, 14·33 per cent)

p-*Aminobenzylsulphonyl-2-aminopyridine.*—The reduction of the above nitro compound did not proceed satisfactorily with ammonium sulphide due to its low solubility. It, was, however; reduced by sodium sulphide or tin (only a slight excess of tin used) and hydrochloric acid. It was a pale pellow, microcrystalline powder, crystallising from hot water, m.p. 1 5-90° after softening at about 120°. (Found : N, 15·9. $C_{12}H_{13}O_2N_3S$ requires N, 16·0 per cent).

N-(p-*Nitrobenzylsulphonyl*)-*sulphanilamide*.—Sulphanilamide (1·72 g.) and p-nitrobenzylsulphonyl chloride (2·4 g.) were ground together and the orange-red product was heated in pyridine for a few minutes. It was then neutralised by adding dilute acid and the separated solid was purified by thrice crystallisation from acetic acid, m.p. 199-200°. (Found : N, 11·3. $C_{13}H_{13}O_6N_3S_2$ requires N, 11·32 per cent). It is very soluble in acetone and pyridine, moderately in alcohol and acetic acid, and sparingly in hot water.

N-(p-*Aminobenzylsulphonyl*)- *sulphanilamide* was obtained by the reduction of the above nitro compound by means of tin and hydrochloric acid similar to the method already described. The hydrochloride crystallised from alcohol, m.p. 175-80° (decomp) and the free base was obtained by decomposing it with dilute ammonia and crystallising it from hot water. It melts at 162·65° after softening. (Found : N, 12·0. $C_{13}H_{15}O_4N_3S_2$ requires N, 12·32 per cent).

Di-p-Nitrobenzylsulphonamide was obtained by heating two molecules of p-nitrobenzylsulphonyl chloride with just the quantity of ammonia or by grinding together with the required amount of ammonium carbonate It was crystallised from dilute alcohol in big prismatic plates, m.p. 268° (decomp.) readily soluble in water (Found : N, 9·9. $C_{14}H_{13}O_8N_3S_2$ requires N, 10·12 per cent).

Di-p-aminobenzylsulphonamide was prepared by reducing the above nitro compound by means of sodium sulphide (2 mols.) in the usual manner, or by tin and hydrochloric acid when a crystailine hydrochloride of the substance was obtained (the reaction was carried out in a similar manner to that described for the preparation of p-aminobenzylsulphonanilide). It decomposed without melting at about 275° and yielded the free amino compound when just neutralised with ammonia. The free diamino compound crystallised from hot water in almost colourless needles and decomposed without melting. (Found: N, 11·6. $C_{14}H_{17}O_4N_3S_2$ requires N, 11·83 per cent).

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STRYCHNINE AND BRUCINE. PART V. SOME DERIVA-TIVES OF DINITRO*ISO*STRYCHNIC ACID.

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Dinitro*iso*strychnic acid is monobasic in character, and it furnishes methyl, ethyl and propyl esters which give crystalline salts. The methiodide of the methyl ester gives N·(b)-methyldinitro*iso*strychnic butaine and the ethyl ester yields by the action of hydrazine hydrate besides a normal hydrazide, two other products of the composition $C_{21}H_{21}O_6N_5,H_2O$ and $C_{21}H_{23}O_5N_5,$ $\frac{1}{4}H_2O$.

In Part III of this series dinitrostrychnic acid was prepared by the action of 5% nitric acid on strychnine and this was treated with 1% potassium hydroxide and piperidine in order to obtain an insight into the orientation of the molecule and a definite information regarding the state of combination of the λ-carbon atom of the indole nucleus. It seemed that by this treatment dinitrostrychnic ·acid might suffer hydrolytic fission

between N(a) and the aromatic nucleus and thus offer a means of determining whether the C atom attached to N(a) is secondary or tertiary. By the action of aqueous alkali on dinitrostrychnic acid, a product is obtained which is considered for some time to be an isomer of the acid or the salt of the phenol after cleavage had occurred in the molecule. To decide this it was necessary to examine dinitro*iso*strychnic acid by comparing some of its derivatives with those of dinitrostrychnic acid. The present investigation shows clearly that alkali treatment does not produce an isomer. The methyl, ethyl and propyl esters and their salts are not identical and one interesting thing in the melting points of the esters is observed. The melting points of the esters of dinitrostrychnic acid rise from methyl, ethyl to propyl, while the m. p. of the isomer goes down likewise as the following table shows,

Esters of dinitrostrychnic acid.		Esters of dinitro*iso*strychnic acid.	
	m.p.		m.p.
Methyl ester	... 210-211°	Methyl ester	... 225°
Ethyl ester	... 226°	Ethyl ester	... 195°
Propyl ester	.. 246°	Propyl ester•	. 118-22°

The action of hydrazine hydrate also differs on the two acids. In the case of dinitrostrychnic acid normal hydrazide is obtained, while the isomer gives besides a normal hydrazide, two other products of the composition $C_{21}H_{23}O_6N_5, H_2O$ (m.p. 221°) and $C_{21}H_{23}O_5N_5, \frac{1}{4}H_2O$ (m.p. 161°). The action of piperidine on ethyl ester does not produce any change and the ester is recovered quantitatively, while nitrous acid gives only a nitrite. The methyl ester follows the normal course in giving N(*b*)-methyldinitrostrychnic-betaine *via* methiodide and chloride. All the esters and their derivatives give well defined crystalline salts.

EXPERIMENTAL.

Methyl Dinitroisostrychnate.—A mixture of dinitroisostrychnic acid nitrate (2 g.), prepared as mentioned in part IV of this series, methyl alcohol (50 c.c.) and concentrated sulphuric acid (2·5 c.c.) was kept gently simmering over a free flame for 7 hours when the substance gradually dissolved to an orange-red solution and was then boiled down to 8 c.c. On adding a few drops of acetic acid methyl dinitro*iso*strychnate crystallised in long needles. Its acetic acid solution on basification with sodium carbonate (the brownish yellow impurities neglected) gave a bright yellow precipitate which was dissolved in chloroform. The solution was washed with water, dried over anhydrous sodium sulphate and concentrated to 5 c.c. On adding methyl alcohol to the solution methyl dinitro*iso*strychnate was obtained in dull yellow prisms. It dissolves readily in chloroform, sparingly in methyl and ethyl alcohol and is insoluble in ether and petroleum ether. It crystallised from ethyl acetate, benzene and acetone in prisms, m.p. 225° (softening at 218°). On drying in *vacuo* at 100° it suffers no loss in weight and shows the presence of one methoxyl group. (Found in anhydrous material: C, 57·5, 57·5; H, 5·3, 5·4; N, 12·1, 12·0; OMe, 8·0. $C_{22}H_{24}O_7N_4$ requires C, 57·9; H, 5·3; N, 12·3; OMe, 7·0 per cent).

The *sulphate* (needles) dissolves in hot water and sparingly in ethanol. It chars at 280-90°. (Found in material dried at 100° in *vacuo*: C, 47·0; H, 5·4; OMe, 4·0. $C_{22}H_{24}O_7N_4 \cdot H_2SO_4, \frac{1}{2}H_2O$ requires C, 46·7; H, 5·0; OMe 5·5 per cent).

The *hydrochloride*, obtained as long prisms by adding hydrogen chloride in ether to a chloroform solution of the base, is soluble in methanol. It chars at 225-35° (softening at 194°). (Found in material dried at 100° in . *vacuo* : Cl, 6·5.: $C_{22}H_{24}O_7N_4$,HCl requires Cl, 7·2 per cent).

The *picrate*, obtained as a bright yellow flocculent mass by adding ethereal picric acid to a chloroform solution of the base, turns into a bright yellow powder on boiling with methanol. It is sparingly soluble in alcohol and water, m.p. 259° (decomp.).

The *methiodide*.—To methyl dinitro*iso*strychnate (0·5 g.), dissolved in dry chloroform (15 c.c.), methyl iodide (0·5 g.) in chloroform (10 c.c.) was added and from the clear orange-red solution a sticky reddish product separated. The reactants were left well corked overnight at room temperature when the mass crystallised in thin needles. After adding ether the crystalline methiodide was collected and washed with chloroform and ether. It is soluble in ethanol and water, m.p. 276-80° (decomp.). After drying at 100° in *vacuo* it suffered no loss in weight, and showed the presence of one methoxyl and one N-methyl group. (Found in anhydrous material : C, 46·4 ; H, 4·9; N, 9·3; OMe, 5·0; NMe, 4·8; I, 21·1. $C_{22}H_{24}O_7N_4$,MeI requires C, 46·2 ; H, 4·5, N, 9·4; OMe, 5·2 ; NMe, 4·8 ; I, 21·1 per cent).

N(b)-Methyl Dinitroisostrychnic Betaine.—An aqueous solution of the methiodide, when treated with freshly precipitated silver oxide, turned red. The filtered solution on concentration turned yellow and deposited thin needles of the betaine which were collected and washed with a little water and alcohol. It is soluble in hot water but insoluble in ethanol and other common organic solvents and does not melt below 325°. It showed the presence of one N-methyl group and was free from methoxyl group (Found in material dried at 100° in *vacuo* : C, 55·0; H, 5·2; N, 11·0; NMe, 5·8. $C_{22}H_{25}O_7N_4$, 1½H_2O requires C, 54·5 ; H, 5·8 ; N, 11·6; NMe, 6·0 per cent).

The *picrate*, prepared in aqueous solution as pale yellow mass, turns into closely packed bunches of needles on rubbing with methanol. It is soluble in warm alcohol and water and gradually decomposes at 259°.

Ethyl Dinitroisostrychnate.—Dinitro*iso*strychnic acid was esterified with 5% ethyl alcoholic sulphuric acid. Addition of ether deposited ethyl dinitro*iso*strychnate sulphate in short stout prisms. A further yield was obtained from the filtrate after removal of the solvent. The sulphate was

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converted into ethyl ester base and its chloroform solution on concentration and addition of ethanol precipitated the ester in cubes. It also crystallises from ethyl acetate, acetone, benzene and ethanol in prisms and is insoluble in ether and petroleum ether, m.p. 195° (softening at 192°). After drying at 100° it was analysed and showed the presence of one OEt group. [Found : C, 58·1 ; H, 6·1 ; N, 11·5 ; OEt, 11·0. $C_{23}H_{26}O_7N_4$ requires C, 58·7 ; H, 5·5 ; N, 11·9 ; OEt (for 1), 12·1 per cent].

The *sulphate* is easily soluble in water and dissolves sparingly in ethanol. It crystallises from dilute alcohol in prisms which decomposed at 250° (frothing at 150°).

The *hydrochloride*, obtained in prismatic plates by adding ethereal hydrogen chloride to a chloroform solution of the base, is soluble in alcohol and water and gradually decomposes at 247°.

The *picrate*, prepared in ether-chloroform solution as bright yellow flocculent mass, on washing with a little chloroform and methanol turned into pale yellow needles, soluble in alcohol and water, m. p. 261° (decomp).

Action of Piperidine on Ethyl Dinitroisostrychnate.—Ethyl dinitro-*iso*strychnate (0·6 g.) was refluxed in dry dioxan (60 c.c.) with piperidine (1 g.) for 4 hours. The red solution on dilution with water gave a flocculant precipitate (0·5 g.) which on recrystallisation had m.p. 153-55°. The filtrate further gave a crystalline product (0·05 g.), m.p. 168°, but neither of the two fractions gave any depression with the original substance, and thus they appear to be its hydrates.

Action of Nitrous Acid on Ethyl Dinitroisostrychnate.—To ethyl dinitro-*iso*strychnate (0·6 g), dissolved in hydrochloric acid (15 c.c., 10%), a solution of sodium nitrite in a few drops of water was added with ice cooling and shaking. On leaving the mixture well corked overnight the nitrite of the ester separated in lemon-yellow needles which on recrystallisation melted at 198-99°. (Found in material dried at 100° in *vacuo* : N, 12·68. $C_{23}H_{26}O_7N_4,HNO_2,H_2O$ requires N, 13·1 per cent). The base from this crystallised in rectangular plates and frothed up at 154-55°. The mixture with the original substance also frothed up at the same temperature. The base was the hydrated form and showed the presence of 1 OEt group. (Found in an undried sample : C, 56·2 ; H, 5·6 ; N. 11·3 ; OEt, 8·0. $C_{23}H_{26}O_7N_4,H_2O$ requires C, 56·6 ; H, 5·7 ; N, 11·5; OEt, 9·2 per cent).

Bromination of Ethyl Dinitroisostrychnate.—The ethyl ester (0·5 g.) was dissolved in dry chloroform (10 c.c.) and to this bromine (0·2 g.) in chloroform (3 c.c.) was added dropwise under ice cooling. On adding ether to the solution a yellow substance separated which crystallised from

methanol-ether mixture in hexagonal prisms, m.p. 200-1°. (Found in an undried sample: Br, 16·6. Found in material dried at 100° in *vacuo*: C, 47·2 ; H, 5·1 ; N, 9·6 ; Br, 16·6. $C_{23}H_{26}O_7N_4Br,2H_2O$ requires C, 47·2 ; H, 5·c ; N, 9·6 ; Br, 13·7 per cent). It was macerated with ammonia and its solution in chloroform after washing and drying gave a sticky residue which could not be induced to crystallise and was, therefore, precipitated with ether in acetone solution. The powder so obtained was soluble in alcohol, acetone and chloroform and gradually melted at 180°. (Found in an undried sample: C, 50·4 ; H, 5·2 ; N, 9·0 ; Br, 14·5; OEt, 9·2. $C_{23}H_{25}O_7N_4Br$ requires C, 50·3 ; H, 4·5 ; N, 10·2 ; Br, 14·6 OEt, 9·6 per cent .

Action of Hydrazine Hydrate on Ethyl Dinitroisostrychnate.—Ethyl dinitro*iso*strychnate (4 g.) was dissolved in butyl alcohol (50 c.c.) and on adding hydrazine hydrate (7 g.) the orange solution turned red. It was refluxed for 45 minutes, when a solid separated after 15 minutes. It was allowed to cool and the crystalline mass collected (3 g.). A further yield (0.5 g.) was obtained on adding acetone to the concentrated solution. The combined crystalline solid was dissolved in methanol when a portion remained undissolved (A). The alcohol-soluble fraction gave a further small yield of (A) besides a crystalline solid which could be separated into acetone-insoluble (B) and acetone-soluble (C) fractions.

Fraction (A): Dinitroisostrychnic Hydrazide.—It was dissolved in methanol under reflux and from the solution on cooling the hydrazide separated as a crystalline mass, insoluble in acetone, benzene, ethyl acetate, ether and chloroform and did not melt below 280° and showed the absence of ethoxyl group. (Found in material dried at 100° in *vacuo*: C, 54·7 ; H, 5·7 ; N, 17·5. $C_{21}H_{21}O_6N_4·NH·NH_2$, $\frac{1}{4}H_2O$ requires C, 54·8 ; H, 5·4 ; N, 18·1 per cent).

Fraction B —This was easily soluble in cold methanol and on adding acetone crystallised in prisms, insoluble in ethyl acetate and benzene and frothed up at 221° (loss at 100°, 7·6% ; $2H_2O$ requires 7·34 per cent). (Found in material dried at 100° in *vacuo*: C, 53·50, 53·4 ; H, 5·7, 5·7 ; N, 15·5. $C_{21}H_{23}O_6N_5$, H_2O requires C, 54·9 ; H, 5·5; N, 15·3 per cent). *The picrate* was obtained in glistening plates, m.p. 225-35° (frothing).

Fraction C.—This was crystallised from methanol in prisms, soluble in chloroform, ethyl acetate, benzene and frothed up at 160°. It was free from ethoxyl group and after drying at 100° in *vacuo* lost 4·5% H_2O (theory requires 4·2%). (Found in dried material : C, 57·2 ; H, 5·7 ; N, 17·4. $C_{21}H_{23}O_5N_5$, $\frac{1}{4}H_2O$ requires C, 57·5 ; H, 5·5 ; N, 15·8 per cent). *The picrate*, prepared in methanol-ether solution, melted at 225-35° (decomp.) (frothing at 178°).

Propyl Dinitroisostrychnate.—Propyl dinitroisostrychnate was also prepared in a similar fashion; the base crystallised on the addition of propyl alcohol to its chloroform solution as prismatic needles, m.p. 118-22°. After drying *in vacuo* at 100° it suffered no loss in weight. (Found : C, 58·0 ; H, 6·5 ; N, 11·3. $C_{24}H_{28}O_7N_4,\frac{1}{2}H_2O$ requires C, 58·4 ; H, 5·9 ; N, 11·4 per cent).

The *sulphate* was sparingly soluble in water and alcohol and was re-crystallised from the former in needles, m.p. 247-48° (decomp.). The *hydrochloride*, prepared in chloroform-ether solution as a sticky mass, crystallised from ethanol in needles, m.p. 225° (frothing) and was sparingly soluble in water. The *picrate*, obtained as a pale yellow powder, was very sparingly soluble in alcohol and water and had m.p. 241-44° (decomp.)

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KOSTANECKI-ROBINSON REACTION. PART I. ACETYLATION OF ORCACETOPHENONE AND ITS MONOMETHYL ETHER.

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Kostanecki acetylation of orcacetophenone and its monomethyl ether gives 4-substituted-C-acylcoumarins. Orcacetophenone on acetylation gives 7-acetoxy-4-acetomethyl-5-methylcoumarin which on treatment with concentrated sulphuric acid yields 7-hydroxy-4-acetomethyl-5-methylcoumarin and the latter on treatment with alkali gives-7-hydroxy-4 : 5-dimethylcoumarin, identical with the product obtained on decarboxylation of the Pechmann condensation product of p-orsellinic acid with ethyl acetoacetate.

Kostanecki reaction, which consists in heating o-hydroxyketones with the sodium salts of fatty acids and anhydrides gives either coumarins or chromones or a mixture of both depending on the ketone, the anhydride and the salt used (Wittig, Bangert and Richter, *Annalen*, 1926, **446**, 155: Bargellini, *Atti. R. Accad. Lincei*, 1925, **2**, 178, 261 ; Heilbron *et al.*, *J. Chem. Soc.*, 1933, 1263 ; 1934, 1311, 1581 ; 1936, 295, *et seq.*).

It has been found in general, that using sodium acetate and acetic anhydride, by the introduction of the higher alkyl substituent-in the side chain of the hydroxyketone, the tendency towards chromone formation increases (Canter, Curd and Robertson, *J. Chem. Soc.*, 1931, 1263 ; Heilbron, Hey and Lythgoe, *ibid.*, 1934, 1581 ; Chadha, Mahal and Venkataraman, *ibid.*, 1933, 1459, *et seq.*).

Keeping the o-hydroxyketone the same, if the anhydride and the sodium salts of higher acids are taken, like propionic and butyric, then there is a tendency towards coumarin formation (Heilbron, Hey and Lythgoe, *loc. cit.* Chakravarti and Majumdar, *J. Indian Chem. Soc.*, 1939, **16**, 151, *et seq.*).

When benzoic anhydride and sodium benzoate or their derivatives are used, the products formed are always flavone derivatives (Allan and Robinson, *J. Chem. Soc.*, 1924, 2192, *et seq.*).

With phenylacetic anhydride or acetic anhydride and sodium phenylacetate, the products formed are always 3-phenylcoumarin derivatives in the case of o-hydroxy-aryl-methylketones (Bergellini, *loc. cit.*; Venkataraman, *et al.*, *J. Chem. Soc.*, 1932, 918 ; 1933, 617, 1459, etc.). In the case of ω-substituted o-hydroxy-aryl-methylketones, chromones are also formed in a small quantity (Baker and Eastwood, *J. Chem. Soc.*, 1929, 2906 ; Heilbron, Hey

and Lythgoe, *loc. cit.*, Chadha, Mahal and Venkataraman, *loc. cit.*). In the case of *o*-hydroxybenzophenones only 4-phenylcoumarin derivatives are formed (Canter, Martin and Robertson, *J. Chem. Soc.*, 1931, 1881 ; Chadha, Mahal and Venkataraman, *loc. cit.*).

Resacetophenone on heating with sodium acetate and acetic anhydride yielded 7-hydroxy-2-methyl-3-acetylchromone which is deacetylated to 7-hydroxy-2-methylchromone (Kostanecki and Rozycki, *Ber.*, 1901, **34**, 102). Kostanecki acetylation of orcacetophenone was, therefore, thought of as a method for the synthesis of 7-hydroxy-2 : 5-dimethylchromone which was required for comparison with the product which resulted on decarboxylation of the product obtained on Pechmann condensation of *p*-orsellinic acid with ethyl acetoacetate (Sethna and Shah, *J. Indian Chem. Soc.*, 1940, **17**, 211).

Orcacetophenone on heating with sodium acetate and acetic anhydride gives a product $C_{15}H_{14}O_5$ (A), m.p. 125-26°, which on treatment with alkali affords $C_{11}H_{10}O_3$ (C), m.p. 248-50°. This has been found on direct comparison to be the same as 7-hydroxy-4:5-dimethylcoumarin (I, R = R′ = H) (Sethna and Shah, *loc. cit.*).

The molecular formula of the product (A) differs from that of (C) by $C_4H_4O_2$ which suggests the presence of two acetyl groups, one of which of course must be the *O*-acetyl group, the other being a *C*-acetyl group. Attempts were directed towards the stepwise elimination of the *O*-acetyl and *C*-acetyl groups. Alkali of varying strength fails to give the desired result. However, on treatment of the product (A) with concentrated sulphuric acid a product (B), $C_{13}H_{12}O_4$, m.p. 214°, has been isolated which on treatment with dilute alkali gives (C). Both the products (A and B) give 2:4-dinitrophenyl-hydrazones which shows the presence of a *C*-acetyl group. The fact that it is easily split off with alkali as well as the fact that the product (B) gives no colouration with alcoholic ferric chloride show that it must be in the pyrone ring. The production of 7-hydroxy-4:5-dimethylcoumarin (I, R = R′ = H) from (B) with the loss of an acetyl group shows that there must be a methyl group in the posiqition 4 after deacetylation. This suggests two alternative structures, 7-hydroxy-3-acetyl-4:5-dimethylcoumarin (II) and 7-hydroxy-4-acetomethyl-5-methylcoumarin (I, R = H ; R′ = COMe) for (B). The latter structure is provisionally assigned to (B) because there is no conceivable mechanism by means of which the presence of an acetyl group in position 3 can be accounted for. Hence (A) is (I, R = R′ = COMe).

It may be noted that the *C*-acetyl group could not be introduced by the action of sodium acetate and acetic anhydride under the conditions of Kostanecki reaction on 7-hydroxy-4:5-dimethylcoumarin.

The following mechanism is suggested for the formation of 7-acetoxy-4-acetomethyl-5-methylcoumarin.

The first step is the formation of the diacetyl derivative of orcacetophenone (i). This is then converted into the β-diketone (ii). The acetyl derivative of the β-diketone (iii) then gives on ring-closure 7-acetoxy-4-acetomethyl-5-methylcoumarin (I, R = R′ = COMe)

The monomethyl ether of orcacetophenone gives on similar acetylation 7-methoxy-4-acetomethyl-5-methylcoumarin, identical with the methyl ether of (I, R = H; R′ = COMe) which on treatment with alkali gives 7-methoxy-4:5-dimethylcoumarin, identical with the methyl ether of (I, R = R′ = H).

The exclusive formation of a coumarin in the Kostanecki reaction on orcacetophenone and its monomethyl ether is a point of interest as the acetylation of o-hydroxyacetophenones produces either exclusively a chromone or a mixture of chromone and coumarin (Kostanecki and Rozycki, loc. cit.; Wittig, Bangert and Richter, loc. cit.). The 6-methyl group in orcacetophenone, therefore, seems to have a profound influence on the course of the Kostanecki reaction.

Attention may be also drawn to the new technique in which the O-acetyl group is hydrolysed with concentrated sulphuric acid which leaves the C-acetyl group in the pyrone ring absolutely intact and which is then removed with alkali. This new technique of stepwise elimination of O-acyl and C-acyl

groups promises to be of use in the isolation of 3-acylchromones, and the work to study the applicability of this method in the synthesis of coumarins and chromones is in progress.

Experimental.

7-Acetoxy-4-acetomethyl-5-methylcoumarin   (I, R = R′ = COMe).— Orcacetophenone (10 g.), prepared by Hoesch's method (*Ber.*, 1915, **48**, 1127), sodium acetate (30 g.) and acetic anhydride (100 c.c.) were refluxed in an oil-bath at 180–90° for 8-9 hours. The excess of acetic anhydride was distilled off and the reaction mixture added to water. The solid obtained gave on crystallisation from rectified spirit long wooly needles (6·5 g), m.p. 125-26°. (Found: C, 65·8; H, 5·3. $C_{15}H_{14}O_5$ requires C, 65·7 ; H, 5·1 per cent).

The 2:4-*dinitrophenylhydrazone*, prepared from the above product and 2:4-dinitrophenylhydrazine hydrochloride as usual, was crystallised from glacial acetic acid in tiny yellow needles, m.p 238-39°. (Found: N, 12·2. $C_{21}H_{18}O_8N_4$ requires N, 12·3 per cent).

7-Hydroxy-4-acetomethyl-5-methylcoumarin (I, R=H ; R′=COMe).— The product (I, R=R′=COMe) (1 g.) was kept for 4 hours with concentrated sulphuric acid (10 c.c.) and then the reaction mixture added to cold water. The product, which separated, was crystallised from rectified spirit in tiny shining needles (0·7 g.), m.p. 214°. It gives no colouration or fluorescence with alkali or concentrated sulphuric acid. It also gives no colouration with alcoholic ferric chloride. (Found: C, 67·1 ; H, 5·2. $C_{13}H_{12}O_4$ requires C, 67·2 ; H, 5·2 per cent).

The 2:4-*dinitrophenylhydrazone*, prepared as usual, was crystallised from rectified spirit in yellow needles, m.p. 250-60° (decomp.). (Found: N, 13·0. $C_{13}H_{16}O_7N_4$ requires N, 13·6 per cent).

The *methyl ether*, prepared as usual by refluxing the acetone solution of (I, R=H ; R′=COMe) with fused potassium carbonate and methyl iodide was crystallised from dilute alcohol in long shining needles, m.p. 123-24°. (Found: C, 68·5 ; H, 5·6. $C_{14}H_{14}O_4$ requires C, 68·3, H, 5·7 per cent).

7-Hydroxy-4:5-dimethylcoumarin (I, R=R′=H).—The product (I, R= H; R′=COMe) (1 g.) was shaken up with sodium hydroxide (5%, 15 c.c.) and kept for 3 hours. The product obtained on acidification with hydrochloric acid was crystallised from rectified spirit in stout shining needles (0·7 g.), m.p. 248-50°. Mixed m.p. with 7-hydroxy-4:5-dimethyl coumarin (Sethna and Shah, *loc. cit.*) was not depressed.

Deacetylation can also be effected by refluxing the products (I, R=R′= COMe) and (I, R=H ; R′=COMe) with sodium carbonate solution (5·5%) for about 1½ hours. The yield is, however, inferior,

The product (I, R=R'=COMe) on treatment with dilute sodium hydro-xide gives directly (I, R=R'=H) and the product (I, R=H ; R'=COMe) cannot be isolated.

The *methyl ether*, prepared from the *acetone* solution of (I, R=R'=H) methyl iodide and fused potassium carbonate was crystallised from dilute alcohol in needles, m.p. 117-19°, mixed m.p. with 7-methoxy-4:5-dimethyl-coumarin (Sethna and Shah, *loc. cit.*) was not depressed.

The *acetyl derivative*, prepared as usual, was crystallised from rectified spirit in silky needles, m.p. 119-120°. Mixed m.p with 7-acetoxy-4:5-dimethylcoumarin (Sethna and Shah, *loc. cit.*) was not depressed.

With a view to see if the *C*-acetyl group can be introduced in the pyrone ring of (I, R=R'=H) the compound (I, R=R'=H) (0·3 g.) was heated with acetic anhydride (10 c.c.) and sodium acetate (1 g.) for 8 hours at 180-90°. The excess of acetic anhydride was distilled off and the reaction mixture was poured into water. The product obtained on crystallisation from dilute alcohol gave silky needles, m.p. 119-20°. Mixed m.p. with the above acetyl derivative from (I, R=R'=H) was not depressed, Mixed m p. with the product (I, R=R'=COMe) was depressed by 15°.

Acetylation of Orcacetophenone Monomethyl Ether : 7-Methoxy-4-aceto-methyl-5-methylcoumarin.—Orcacetophenone monomethyl ether (2 g.), sodium acetate (6 g.) and acetic anhydride (20 c.c.) were refluxed for 8 hours at 180-90°. The product obtained on crystallisation from rectified spirit gave glistening needles, m.p. 122-23°. Mixed m.p. with the methyl ether of 7-hydroxy-4-acetomethyl-5-methylcoumarin was the same.

This methyl ether (0·5 g.) was kept in contact with sodium hydroxide (5%; 10 c.c.) for 3 hours. The product, obtained on acidification, was crystallised from dilute alcohol in needles, m.p. 117-19°. Mixed m.p. with 7-methoxy-4:5-dimethylcoumarin (*loc. cit.*) was the same.

All the analyses recorded are micro-analyses.

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ACRIDINE DERIVATIVES. PART V. AUROTHIO- AND ARGENTOTHIO-ACRIDINES.*

By S. J. DAS-GUPTA.

Gold and silver compounds of 5-thiolacridine derivatives have been described.

It was considered to be of interest to prepare acridine compounds with gold or silver and note their pharmacological activity. For this purpose, 5-thiolacridine derivatives of the type (I, R=H) have been prepared. These thiolacridines, on treatment with potassium auribromide, afford the gold compounds of the type (I, R=Au). The silver compounds of the type (I, R=Ag) are prepared by treating the sodium salts of the thiolacridines with silver nitrate.

The 5-thiolacridine derivatives readily dissolve in sodium hydroxide solution and may be regenerated from these solutions by neutralisation. But the products liberated are lighter in colour than the parent compounds. Recrystallisation or simple heating on a steam-bath transforms them back to the original form. This suggests that most probably the thiolacridine derivatives exist in both thio-ketonic (II) and thio-enolic forms (III).

All the gold and silver compounds are stable and deep red coloured solids having definite melting points. They are insoluble in water and in common organic solvents.

During the preparation of the above aurothioacridines, another set of gold compounds has been isolated possessing a lighter colour. From general properties and the results of analysis, the structure (IV) is assigned to them.

Previous parts of this series of papers appeared under the caption "Acridine derivatives as antimalarials".

EXPERIMENTAL.

2-Chloro-7-methoxy-5-thiolacridine.—2 : 5-Dichloro - 7 - methoxyacridine (2 g.) was heated with potassium xanthogenate (4 g.) in phenol (6 g) at 115° for 3 hours. After cooling, the mixture was poured into ice-cold water, stirred for some time, filtered and washed thoroughly with water, and crystallised from alcohol in deep red shining needles, m.p. 245°. The substance is insoluble in water but soluble in both aqueous and alcoholic sodium hydroxide solution. On acidification of alkaline solution, the thiol compound is precipitated as yellow needles but may be reconverted to the red variety when heated in a steam-oven or when recrystallised from alcohol. The yellow form, admixed with equal part of the red variety, melts at 245° without depression. (Found : N, 4·98 ; S, 11·4. $C_{14}H_{10}ONClS$ requires N, 5·08; S, 11·61 per cent).

2-Chloro-7-methoxy-5-aurothiolacridine (Structure analogous to I).—To 0·55 g. of 2-chloro-7-methoxy-5-thiolacridine in alcohol (25 c.c.), sulphur dioxide solution (4%, 20 c.c.) was added and the mixture was slowly treated at room temperature with a solution of potassium auribromide (1·2 g.) in alcohol (12 c.c.). The mixture was allowed to stand for several hours with occasional shaking and then diluted with alcohol, filtered, and the product washed thoroughly with alcohol and water. The dark red amorphous substance was dried in *vacuo* over phosphorus pentoxide, m.p. 247-48° (decomp.). It is very sparingly soluble in acetone and insoluble in all other common solvents and could not be further crystallised. It is also insoluble in dilute acids but sparingly soluble in hot and strong hydrochloric and acetic acids. (Found : N, 3·18 ; S, 6·27 ; Au, 43·2. $C_{14}H_9ONClSAu$ requires N, 2·97 ; S, 6·78 ; Au, 41·78 per cent).

Bromoauro-5-dithio-(2-chloro-7-methoxy)-acridine (Structure analogous to IV).—2-Chloro-7-methoxy-5-thiolacridine (crystallised, 0·55 g.) in alcohol (25 c.c.) was treated slowly with a solution of potassium auribromide (0·6 g.) in alcohol (10 c.c.). Sulphur dioxide solution (4%, 6 c.c.) was then added slowly and the mixture left aside for several hours with occasional shaking. After dilution with alcohol, the mixture was filtered, washed thoroughly with alcohol and water. The solid, after being dried in *vacuo*, was obtained as a deep red amorphous substance, m.p. 254-55° (decomp). It is very sparingly soluble in alcohol and acetone and in all other solvents and dilute acids. [Found : N, 3·44 ; S, 7·88 ; Au, 23·3. $(C_{14}H_9ONClS)_2 AuBr$ requires N, 3·39 ; S, 7·75 ; Au, 23·85 per cent].

2-Chloro-7-methoxy-5-argentothiolacridine.—2-Chloro-7-methoxy-5-thiolacridine (1·1 g.) was dissolved in dilute alcohol (50 c.c.) containing sodium hydroxide (0·16 g.) and silver nitrate solution (0·75 g. in 10 c.c. of water)

was added slowly with shaking when a precipitate separated out. After a few minutes the solid was collected, washed thoroughly with alcohol and water, and dried in *vacuo*. The dark red amorphous substance, m.p. 290° (decomp.), thus obtained, is almost insoluble in all common solvents and in ammonia and dilute acids but is sparingly soluble in strong acids. (Found : N, 3·54; Ag, 28·26. $C_{14}H_9ONClSAg$ requires N, 3·66 ; Ag, 28·23 per cent).

7-Methoxy-5-thiolacridine.—7-Methoxy-5-chloroacridine (2 g.) and potassium xanthogenate (4 g.) were heated in phenol (6 g.) at 125-30° for more than 3 hours. Isolated as described previously, the compound was obtained in red shining needles from alcohol, m.p. 231-32°. (Found : S, 13·07. $C_{14}H_{11}ONS$ requires S, 13·27 per cent). It is insoluble in water but soluble in dilute aqueous or alcoholic sodium hydroxide solution, from which it is liberated on acidification in light yellow form with identical melting point and changes to the red variety when heated in a steam-bath or when recrystallised.

7-Methoxy-5-aurothioalcridine.—The above thiolacridine (0·48 g.) in alcohol (20 c.c.) was mixed with sulphur dioxide solution (20 c.c., 4%) and then slowly treated with an alcoholic solution of potassium auribromide (1·2 g.). Isolated as in the previous case, the compound was obtained as dark red amorphous powder, insoluble in all common solvents, m.p. 219-20° (decomp.). (Found : S, 7·01 ; Au, 46·7. $C_{14}H_{10}ONSAu$ requires S, 7·32 ; Au, 45·08 per cent).

Bromoauro-5-dithio-(7-methoxy)-acridine (Structure analogous to IV).—The foregoing thiolacridine (0·48 g.) in alcohol (20 c.c.) was slowly treated with an alcoholic solution of potassium auribromide (0·6 g.). The mixture was shaken and sulphur dioxide solution (6 c.c., 4%) was slowly added. The compound was isolated as a deep red powder, m.p. 222-23°. [Found : S, 8·45 ; Au, 27·0. $(C_{14}H_{10}ONS)_2$ AuBr requires S, 8·25 ; Au, 26·02 per cent].

7-Methoxy-5-argentothiolacridine.—The thiolacridine was dissolved in dilute alcohol containing equivalent proportion of sodium hydroxide and treated with silver nitrate as described. The compound was isolated as brick-red amorphous powder, insoluble in all solvents, m.p. 261° (decomp.). (Found : N, 3·89 ; Ag, 31·12. $C_{14}H_{10}ONSAg$ requires N, 4·02; Ag, 31·03 per cent).

NUTRITION STUDIES IN BIHAR. PART III. ESTIMATION OF CAROTENE AND ASCORBIC ACID IN COMMON FRUITS AND VEGETABLES.

BY K. MITRA H. C. MITTRA AND A. C. ROY.

The carotene and ascorbic acid content of various leafy and other vegetables and fruits commonly grown in Bihar have been estimated chemically. Of the fruits analysed ripe Barhar (*Artocarpus lakoocha*) and the juice of the ripe palmyra fruits have been found to be very rich in carotene. Another vegetable having exceedingly high ascorbic acid content has been Chathail (*Momordica cochinchinensis*). The leafy vegetables analysed gave high carotene and ascorbic acid values.

The literature on the importance of carotene and ascorbic acid in human nutrition is steadily growing in volume. In the absence of a comprehensive table of food values field workers engaged in dietary survey experience difficulty in assessing the complete value of daily intake (comprising of diverse edibles) in terms of proximate principles of food, particularly the different vitamins.

Inspite of the slight (at times negligible) variability inevitably associated with animal experiments, biological assay is still accepted as the standard method as far as the vitamins are concerned. But the chemical methods of assessment have been receiving more and more attention from workers all over, being quicker, less complicated and more economical. As regards ascorbic acid the chemical methods of estimation inspite of its slight drawbacks has been universally accepted. With carotene, the methods have yet to be perfected but for ordinary purposes of dietary study and propaganda, the chemical methods have their uses.

EXPERIMENTAL.

Carotene.—The extraction of carotene from the vegetables and fruits was done exactly by the technique described by Ahmed *et al (Indian J. Med. Res.,* 1937, **24**, 801) but the estimation of the ethereal extract containing the carotenoid pigment was done by colour comparison method advocated by Guilbert (*Ind. Eng. Chem. Anal. Ed.,* 1934, **6**, 452) and subsequently modified by Petersen *et al (ibid.,* 1937, **9**, 71). The latter method eliminates the use of Lovibond tintometer and more commonly available colorimeter is used instead. The stock dye solution was made

by dissolving naphthol yellow (3.06 g.) and Orange-G crystals (0.45 g.) in one litre of water. The stock dye solution (5 c. c.) was further diluted to 1 litre and this constituted the standard dye solution, the colour of which matched with a solution containing 2.4 mg. of β-carotene per litre. Banerji and Ramasarma (*Agric. & Live-stock in India*, 1938, **8**, 253) have used potassium dichromate as the standard dye solution, but the authors found the former dye standard as efficient as the latter by duplicate set of experiments. It was further observed that in removal of xanthophyll, ethyl alcohol worked as efficiently as its next lower homologue, the latter being advocated by Guilbert (*loc. cit.*).

Ascorbic Acid.—The estimation of ascorbic acid was made by dichlorophenol-indophenol titration method (Birch *et al.*, *Biochem. J.*, 1933, **27**, 590) with the addition of pyrophosphate as advocated by Giri (*Indian J. Med. Res.*, 1938, **26**, 166). Considerable difficulty was experienced in the determination of the end-point (in titration) if the juice extracted from fruits or vegetables was highly coloured. Wherever necessary, blank control titrations were made simultaneously but this method did not work if the extracted juice showed slightest red tinge. Consequently all doubtful results have been left out of the table below. In such cases extractions made with metaphosphoric acid on the lines recently advocated by Lanke (*Skand. Arch. Physiol.*, 1939, **81**, 300) may help future workers to determine the end-point with some amount of precision.

TABLE I.

Leafy vegetables.

Figures are given in mg. per 100 g. of the material.

No.	Hindi name.	Eng. name.	Bot. name.	Carotene.	Ascorbic acid.
1	Alu sag*	Tender stalks of potato.	*Solanum tuberosum*	12.2 mg.	73.6 mg.
2	Bathua sag	Goose foot	*Chenopodium album*	12.4	65.4
3	Boont sag	Tender Bengal gram plant.	*Cicer arietinum*	18.4	199.8
4	Dhania sag	Coriander plant	*Coriandrum sativum*	11.6	82.2
5	Gajar sag	Stalk of carrot.	*Daucus carota*	14.8	92.8

* *Sag* means tender leaves and stem of the plant unless otherwise mentioned.

Statements within bracket gives the character of the edible and not specific names.

TBALE I (contd.).

No. Hindi name.	Eng. name.	Bot. name.	Carotene.	Ascorbic acid.
6 Gendhari sag	Love-lies-bleeding	*Amaranthus caudatus*	14·8	77·3
7 Kachnar ka patta	(Leaves only)	*Bauhinia variegata*	8·4	69·6
8 Kaddoo sag	Bottle gourd	*Lagenaria vulgaris*	9·7	33·0
9 Kalmi sag	Ipomea	*Impomœa sepiaria*	10·8	43·7
10 Kanta gendhari sag	Thorny pigweed leaves	*Amaranthus spinosus*	26·8	133·9
11 Kelao ka patta	Tender leaves of pea only	*Pisum arvense*	24·4	105·7
12 Kelao sag	Tender pea leaves & stem	Do	15·5	109·4
13 Khesari sag	Tender lathyrus	*Lathyrus sativus*	15·5	81·3
14 Konhra sag	Pumpkin	*Cucurbita maxima*	10·1	38·7
15 Lahsun ka patta	Green stalks of garlic	*Allium sativum*	4 2	94·1
16 Lal sag	Red pigweed	*Amaranthus rubrum*	11·5	?
17 Lofa sag	...	*Malva verticillata*	7·5	43·3
18 Methi sag	Fenugreek	*Trigonella foenum-graecum*	9·1	92·0
19 Mnrai sag	Stalk of radish	*Raphanus sativus*	7 4	126·4
20 Palki sag	Spinach	*Spinacia oleracea*	6·1	41·2
21 Parwar sag	...	*Trichosanthes dloica*	13·4	110·2
22 Patua sag	Tender leaves & stem of jute	*Corchorus capsularis*	10·8	66·2
23 Piyaz ka patta	Green stalks of onion	*Allium cepa*	2 0	27·7
24 Podina	Mint	*Mentha viridis*	8·7	?
25 Pooin sag	...	*Bassella rubra*	4·8	79·4
26 Salad ka sag	Lettuce	*Lactuca sativa*	6·8	50·9
27 Sarso sag	Rape seed leaves	*Brassica napus*	8·8	118·3
28 Sowa sag	Sowa	*Peucedanum sowa*	15·0	77·5

TABLE II.

Other vegetables.

[Figures are given in mg. per 100 g. of material]

No.	Hindi name.	Eng. name.	Bot. name.	Carotene.	Ascorbic acid.
1	Bakala	...	*Vicia faba*	0·9	30·1
2	Barsema	Sword bean	*Canavalia ensiformis*	0·2	25·0
3	Chalta	...	*Dillenia indica*	0·1	9·0
4	Chathail or kheksa (big)	Hilly variety	*Momordica cochin chinensis*	0·4	65·0
5	Do (small)	Country variety	Do	1·8	246·9
6	Gajar	Carrot	*Daucus carota*	7·7	25·0
7	Gulcharni	(Flower stalks)	*Calonyction muricatum*	0·6	19·1
8	Gullar	Figs	*Ficus hispida*	0·3	5·7
9	Jhingi	Ridge gourd	*Luffa acutangula*	0·4	15·8
10	Kachri boont	Tender Bengal gram	*Cicer arietinum*	2·2	73·7
11	Kamrak	...	*Averrhoa carambola*	0·4	30·4
12	Kankari	Gourd fruit	*Cucumis melo var utilissimus*	0·2	16·7
13	Katcha Aam	Green mango	*Mangifera indica*	Trace	43·6
14	Katcha Barhar	...	*Artocarpus lakoocha*	?	32·7
15	Katcha matar (Kabuli matar)	English peas green	*Pisum sativum*	1·2	23·5
16	Matar	Country peas green	*Pisum arvense*	3·1	18·9
17	Katcha papita (chhilka)	Skin of green papaya	*Carica papaya*	2·4	72·4
18	Do. (gudda)	Do. (pulp)	Do	0·4	32·0
19	Katcha arhar ka dana	Tender red gram	*Cajanus indicus*	0·8	29·7
20	Kawachia sem	Cowage	*Mucuna capitata*	0·6	26·8
21	Kelao sag ke danti	Stem of pea	*Pisum arvense*	6·8	47·3
22	Konhra flower	Flower of pumpkin	*Cucurbita maxima*	1·0	22·6
23	Kudrum (patwa)	Roselle or red sorrel	*Hibiscus sabdariffa*	0·4	?

TABLE II (contd.).

Other vegetables.

No.	Hindi name.	Eng. name.	Bot. name.	Carotene.	Ascorbic acid
24	Kundri	...	Cephalandra indica	0·3	21·3
25	Lataru bia	(Vegetable)	Dioscorea alata	0·4	15·1
26	Lataru	(Tuber)	Do.	0·1	16·4
27	Muchkund (Kanak-champa)	...	Pterospermum acerifolium	0.4	18·6
28	Nenua	Vegetable marrow	Luffa aegyptiaca	0·2	10·0
29	Parwar (green)	...	Trichosanthes dioica	0·5	42·4
30	Do (ripe)	...	Do	1·5	?
31	Raharia sem (Guar)	Cluster bean	Cyamopsis psoralioides	1·2	38·1
32	Ramtorai (Bhindi)	Ladies finger	Hibiscus esculentus	0·3	17·4
33	Roma or Boro (red)	Cow pea pods	Vigna catiang	0·6	24·0
34	Do (greenish white)	Do	Do	0·6	28·4
35	Saijan ka phool	Drumstick flower	Moringa oleifera	0·9	142·9
36	Sem	Broad bean (big)	Dolichos lablab	0·3	17·4
37	Do (small)	Do (small)	Do	0·7	17·8
38	Soothny	...	Dioscorea fasciculata	Trace	11·9

TABLE III.

[Figures are given in mg. per 100 g. of material].

Fruits.

No.	Hindi name.	Eng. name.	Bot. name.	Carotene.	Ascorbic acid.
1	Aam Bombai	Mango	Mangifera indica	6·0	10·5 ?
2	Aam sipia	Do	Do	2·6	
3	Amra	Hog plum	Spondios mangifera	0·4	37·6
4	Bael	Wood apple	Aegle marmelos	0·1	4·7
5	Barhar (ripe) (Beng. Mādār)	...	Artocarpus lakoocha	18·0	?
6	Bayr (bara)	Indian plum (sweet)	Zizyphus jujuba	0·5	22·3

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TABLE III (contd.).

Fruits.

No. Vern. name.	Eng. name.	Bot. name.	Carotene.	Ascorbic acid.
7 Bayr (chhota)	Do (small)	Do	0·4	30·5
8 Falsa	...	*Grewia asiatica*	0·3	10·5
9 Gab	...	*Diospyros embry-opteris*	0·2	22·3
10 Jamun	Black berry	*Eugenia jambolana*	0·1	?
11 Kadam	(Inflorescence)	*Anthocephalus cadamba*	2·5	16·5
12 Kaint	Elephant apple	*Feronia elephant-um*	Trace	21·9
13 Kalaonda	(Acid berries)	*Carissa carandus*	0·1	18·4
14 Kend	...	*Diospyros melano-xylon*	0·1	4·1
15 Kesaur	...	*Pachyrhizus angulata*	Nil	25·9
16 Kharbuja	Musk melon	*Cucumis melo*	0·5	12·1
17 Khirni	...	*Mimusops hexan-dra*	1·3	24·2
18 Loquat	Loquat	*Eriobotrya japo-nica*	0·4	?
19 Makoh	Cape goosebery	*Physalis peruviana*	3·4	22·8
20 Pakka papita (chhilka)	Ripe papaya (skin)	*Carica papaya*	4·7	51·4
21 Do (gudda)	do (pulp).	Do	2·8	50·9
22 Piyal	...	*Buchanania latifolia*	1·4	7·7
23 Sarifa	Custard apple	*Anona squamosa*	Nil	36·7
24 Singhara	Water chestnut	*Trapa bispinosa*	Trace	16·3
25 Tarbuja	Water melon	*Citrullus vulgaris*	1·8	7·0
26 Tarh ka pheda	Ripe palmyra fruit (mesocarp)	*Borassus flabellifer*	7·6	24·0
27 Toont hara	Mulberry (green variety).	*Morus indica*	0·2	?
28 Toont lal	Do (red variety)	Do	0·2	?
29 Velowa	Orange cups of marking nut	*Semecarpus ana-cardium*	0·9	41·4

DISCUSSION.

It is quite evident from the above tables that the leafy vegetables are very rich sources of vitamins A and C. Of the 28 kinds of *sags* analysed

the less popular edible leaves *e.g. Boont, Khesari, Kelao* and *Kanta gendha-i sags* were found to exceed in carotene and ascorbic acid content the more popular *palki sag, pooin sag,* or *salad ka sag.* It has further been noticed that leaves of the plants are richer in both the protective elements as compared with their respective stems. The consumption of the tender stems and leaves of jute plant (*Pat sag*) is very popular with the poorer section of people in the Purnea district, otherwise it is a rare commodity in this province. From the results published by Levy *et al* (*South African Med. J.,* 1936, **10**, 699) it appears that common edible leaves of South Africa are richer in vitamin C potency as compared to their homologus in Bihar. The findings of Rudra (*Bicchem J.,* 1936, **30**, 701) could be confirmed in the case of green papaya ; the skin being a richer source of vitamin C than the pulp. In the case of the ripe fruit no such difference could be noticed. Amongst the vegetables *Chathail* or *Kheksa* (*Momordica cochinchinensis*) was found to be an extremely rich source of vitamin C. This vegetable creeper grows in abundance all over the province, though not a very popular article of dietary.

Out of the 29 different fruits analysed for carotene ripe *Barhar* seemed to be an exceedingly rich source. The tree yielding this fruit is ubiquitous in its distribution all over the province The fruits are sweet and slightly acid in taste but are not popular with the middle class people. The juice or the mesocarp of the ripe palmyra fruit was found to be another rich source of carotene. *Bhelowa* or marking nuts are not considered edibles in major part of this province but in Chotanagpur division and in the district of Santal Parganas the orange-coloured calyx of the nut is much coveted by the children. They are eaten raw. During cold months in these districts one often encounters children with dark stains on their lips caused by injudicious bite at the nut (the juice of the nut itself being caustic).

It is by no means pretended that the list is complete. This investigation was started with an idea to emphasise ' the desirability of a better acquaintance with our inexpensive food resources,' consequently the edibles selected for analysis are cheap and easily available.

The authors are indebted to Professor S. S. Chaudhury of the department of Biology, P. W. Medical College, Patna, for taking infinite pains to furnish the botanical names of the majority of the edibles cited in the text. To Lt-Col., S. L. Mitra, I.M.S., Director of Public Health, Bihar, they are grateful for suggestions and encouragement.

MEASUREMENT OF SWELLING AND ELECTROKINETIC POTENTIAL OF FIBRIN AT VARIOUS HYDROGEN ION CONCENTRATIONS.

By B. N. Ghosh and N. C. Mukherjee.

The swelling and electrokinetic potential of fibrin have been measured in dilute solutions of a number of mono and polybasic acids. Except in the case of nitric and hydrochloric acids, no parallelism between swelling and electrokinetic potential was observed.

It is well known that proteins like gelatin, fibrin etc, swell in contact with water and dilute solutions of acids and alkalis. The swelling of protein has been found to be minimum at its iso-electric point and as the p_H of the solution in contact with it increases above or decreases below the iso-electric point, the swelling in each case increases, reaches a maximum and then diminishes again. The theories which have been advanced to account for the swelling of proteins distinguish between two types of swelling : (i) at the iso-electric point and (ii) swelling at hydrogen ion concentrations other than that of the iso-electric point.

The swelling at the iso-electric point is usually attributed to the hydration of the protein micelles. Kat (Koll.-chem. Beih., 1918, 9, 1) measured the heat evolved and the contraction in volume of the gelatin-water system during the swelling of gelatin and emphasised on the close analogy between this process and the dilution of a strong solution of sulphuric acid with water.

According to Lloyd and Moran (Proc. Roy. Soc., 1934, A, 147, 342) the water which is imbibed by iso-electric gelatin is held partly as 'firmly bound' water and partly as 'loosely bound' water. The portion of water which can be squeezed out from the gel at a pressure of 8000 lbs per sq. inch is 'loosely bound' water and the other part which begins to be squeezed out at a pressure of 30,000 lbs per sq. inch of the gel is termed 'firmly bound' water. The swelling of gelatin at hydrogen ion concentrations other than that of the iso-electric point has been attributed by Procter and Wilson (J. Chem. Soc., 1916, 109, 307) and also by Ghosh (ibid., 1928, 711) to the higher concentration of the diffusible ions inside the gel than in the outside solution as a result of Donnan equilibrium.

Tolman and Stern (*J. Amer. Chem. Soc.*, 1918, **40**, 264) measured the swelling of fibrin in dilute solutions of acids and concluded that there must be a close relationship between the swelling and the electrical charge of fibrin micelles. They suggested that as the electrical charge of the protein micelles increases, the force of repulsion between them also increases and this causes increase in swelling. It may be pointed out that the increase in the electrical charge of the protein micelles may increase their hydration as suggested by Pauli (*Biochem. Z.*, 1909, **18**, 368) and this may also be responsible for the observed increase in swelling in dilute acid or alkaline solutions. A simultaneous measurement of swelling and electrokinetic potential of fibrin was therefore undertaken to ascertain if there exists any relation between the swelling and electrical charge of this protein. The results obtained are recorded in this paper.

E X P E R I M E N T A L.

About 100 g. of fibrin (Merck's) were taken in a beaker containing a normal solution of hydrochloric acid and stirred with a glass rod. After 2 hours the supernatant solution was poured off, a fresh solution of normal hydrochloric acid was added, the mixture stirred and after allowing to stand for about two hours, the supernatant solution was again decanted off. This process was repeated about four times. The swollen mass of fibrin was then repeatedly washed with distilled water until the p_H of the wash liquid was nearly the same as that of the distilled water used. The fibrin was then dried under a small electric fan and finely powdered. The sample thus prepared was used in all our experiments.

The swelling was thus measured by placing the fibrin sample (1 g.) in a tall graduated cylinder and covering the mass with 100 c.c. of the dilute acid solution of the requisite conductivity. The acid solution was cooled to 10° before use. The cylinder was placed inside a refrigerator maintained at 10°. The contents of the cylinder were stirred twice at intervals of three to four hours to ensure uniformity of concentration of hydrogen ions throughout the solution. The volume occupied by the given weight of the fibrin after 24 hours was read from the graduations in the cylinder.

The electrokinetic potential was measured by means of an arrangement used by Mukherjee and co-workers (*Nature*, 1922, **110**, 732) and described in detail in a paper by Ghosh and Roy (*J. Indian Chem. Soc.*, 1939, **16** 634). The fibrin was transferred from the cylinder to the U-tube and made to occupy its lower part by pressing with a glass rod having a flattened end.

upper part of the **U**-tube and the connecting tubes were filled with an acid solution having the same conductivity as that of the supernatant liquid. The electro-osmotic velocity U is connected with the electrokinetic potential E by the equation

$$U = \frac{EiD}{4\pi\eta K} \qquad \qquad \dots \ (1)$$

where i is the current, K, the specific conductivity of the liquid filling the pores of the diaphram and D, the dielectric constant and η, the coefficient of viscosity of the solution. For dilute solutions D and η may be assumed to remain constant. Hence the equation (1) can be expressed in the form

$$\frac{U \times K}{i} = E \times c$$

where $c = \dfrac{D}{4\pi\eta}$ and is a constant for dilute solutions.

Therefore, the electrokinetic potential is proportional to $U \times K$. In the following tables U is expressed in cubic centimetres of water flowing through the diaphragm per second, i, the current in amperes and K, the specific conductivity in reciprocal ohms. The results obtained with mono-basic acids are recorded in Table I and those with polybasic acids in Table II.

TABLE I.

Acid.	Sp. conducty.	Swelling.	Current.	Charge.	$U \times 10^4$.	$\dfrac{U \times K}{i}$.
Hydrochloric	$2 \cdot 35 \times 10^{-3}$	8 c.c.	6 m.amp.	Positive	1·34	$5 \cdot 5 \times 10^{-4}$
	$1 \cdot 27 \times 10^{-3}$	7	12	,,	1·46	1·55
	$6 \cdot 9 \times 10^{-4}$	6	7	,,	1·16	1·15
	$4 \cdot 1 \times 10^{-4}$	5	7	,,	1·82	1·07
Nitric	5×10^{-3}	7	10	Positive	0·37	1·85
	$2 \cdot 4 \times 10^{-3}$	8	10	,,	0.85	2·08
	$1 \cdot 02 \times 10^{-3}$	5	8	,,	1.46	1·86
	$5 \cdot 8 \times 10^{-4}$	5	8	,,	1·22	0·8
	3×10^{-4}	4·5	6	,,	0·97	0·48
Trichloro-acetic	7×10^{-3}	3	15	Positive	0·24	1·12
	$3 \cdot 2 \times 10^{-3}$	4·5	15	,,	0·49	1.06
	$1 \cdot 8 \times 10^{-3}$	5·5	15	,,	0·73	0·88

TABLE II.

Acid.	Sp. conducty.	Swelling.	Current.	Charge.	$U \times 10^4$.	$\dfrac{U \times K}{i}$.
Sulphuric	$7\cdot3 \times 10^{-3}$	6 c.c.	15 m.amp.	Positive	2.9	$1\cdot39 \times 10^{-4}$
	$1\cdot5 \times 10^{-3}$	8	15	,,	$1\cdot46$	$1\cdot46$
	$1\cdot2 \times 10^{-3}$	6	11	,,	$1\cdot46$	$1\cdot59$
	7×10^{-4}	6	10	,,	$1\cdot46$	$1\cdot02$
Sulphosalicylic	$7\cdot4 \times 10^{-3}$	9	12	Positive	$0\cdot37$	$2\cdot3$
	$2\cdot7 \times 10^{-3}$	9	$8\cdot5$	,,	$0\cdot73$	$2\cdot3$
	$1\cdot7 \times 10^{-3}$	10	8	,,	2.2	$4\cdot76$
	$1\cdot1 \times 10^{-3}$	11	8	,,	2	$2\cdot75$
Oxalic	$5\cdot5 \times 10^{-3}$	11	14	Positive	$0\cdot24$	$0\cdot935$
	$2\cdot9 \times 10^{-3}$	11	12	,,	$0\cdot73$	$1\cdot74$
	$1\cdot5 \times 10^{-3}$	12	10	,,	$0\cdot37$	$0\cdot55$
	1×10^{-3}	12	10	,,	$0\cdot49$	$0\cdot49$
Succinic	1×10^{-3}	12 c.c.	9	Positive	$0\cdot73$ c.c.	$0\cdot73$
	$4\cdot9 \times 10^{-4}$	13	10	,,	$0\cdot49$	$0\cdot27$
	3×10^{-4}	10	10	,,	$0\cdot37$	$0\cdot11$
	$2\cdot3 \times 10^{-4}$	10	8	,,	0.37	$0\cdot106$
Phosphoric	$5\cdot9 \times 10^{-3}$	16	$10\cdot5$	Positive	$0\cdot85$	$4\cdot84$
	$3\cdot5 \times 10^{-3}$	$17\cdot5$	10	,,	$1\cdot34$	$4\cdot55$
	$2\cdot2 \times 10^{-3}$	$17\cdot5$	8	,,	$1\cdot34$	$3\cdot74$
	$1\cdot4 \times 10^{-3}$	17	8	,,	1.8	$3\cdot08$
	$1\cdot1 \times 10^{-3}$	16	8	,,	$1\cdot93$	$2\cdot64$
	$8\cdot5 \times 10^{-4}$	13	6	,,	$1\cdot82$	$2\cdot6$

DISCUSSION.

It will be noticed from the data recorded in Table I that in the case of the two acids, the hydrochloric and the nitric, as their concentration in solution increases, the swelling of fibrin at first increases, reaches a maximum and then diminishes again. The electrokinetic potential of fibrin also changes in the same way as the swelling, the maximum of swelling occurring at the maximum value of the electrokinetic potential. In the case of trichloroacetic acid, however, with the increasing concentration of

the acid, the electrokinetic potential increases while the swelling decreases. This results leads one to doubt if there is any relation between the swelling and the electrokinetic potential of fibrin.

Again, when the results recorded in Table II are examined, it is noticed that in the case of all the polybasic acids used, the maximum of swelling does not occur all at the same concentration of the solution at which the electrokinetic potential is the maximum. In contact with the solutions of sulphosalicylic acid the swelling decreases as the concentration of the acid increases, while the electrokinetic potential at first increases, reaches a maximum, and then decreases. In the case of succinic and phosphoric acids, as the concentration of their solutions increases the the swelling increases, reaches a maximum and then diminishes again, while the electrokinetic potential continues to increase steadily. It appears from these results that there is no relation between the swelling and the electrokinetic potential of fibrin in contact with solutions of dibasic acids used.

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EFFECT OF BOILING AND FRYING ON THE ENZYMIC HYDROLYSIS OF FISH PROTEIN.

BY K. C. SAHA.

The effects of different methods of cooking, frying and boiling, for different periods of time on the enzyme hydrolysis of the proteins of fish have been studied. The hydrolysis has been carried out *in vitro* by pepsin, trypsin and by pepsin followed by trypsin. The rate of digestion of fish under-cooked in boiling water is greater than that of raw, fried or thoroughly cooked fish. With all the species under investigation, the rate of hydrolysis is found to be greater in peptic digestion than in tryptic, except in two cases *viz.* Boal (*Wallagu attu*) and Shole (*Ophcephalus straitus*) where the results are reversed.

From the nutritional standpoint the art of cooking and its effects on the digestibility and nutritive value of foodstuffs constitute an important problem. According to Hutchinson ("Food and Principles of Dietetics", p. 396), cooking increases the digestibility of vegetable foodstuffs, but decreases that of animal foodstuffs. Heinbecker (*J. Biol. Chem.*, 1928, 80, 462) states that the Eskimo in his native condition eats practically raw flesh and remains healthy. But in those parts, where owing to the spread of civilisation, the Eskimo cooks his meat, health has deteriorated and scurvy occurs. Much work on the effect of cooking on the nutritive value of foodstuffs has been carried out in England by McCance and co-workers.

In the present work the effects of different methods of cooking, frying and boiling for different periods of time on the digestibility of the proteins of fish, which constitutes an important article of diet in Bengal, have been investigated. The digestions have been carried out *in vitro* by pepsin, trypsin and by pepsin followed by trypsin.

EXPERIMENTAL.

The edible portions of the fresh fish samples, purchased from the local market, were cut into small and equal pieces. Each of the pieces from the same part of the body of the same fish was divided into 4 equal portions in order to maintain uniformity as far as possible. Of these four samples (*a*) one was kept raw, (*b*) one was fried in mustard oil till the colour of the fish was dark brown, as is done in the domestic kitchen in Bengal, (*c*) one was cooked for 20 minutes in boiling water and (*d*) one was under-cooked in boiling water for 10 minutes. These are referred to as raw, fried, cooked and under-cooked respectively in the tables which give the averages of the determinations of three samples in each case. After cooking the pieces were allowed to cool, any obvious fat and connective tissue were removed and the remaining portion was minced in an 'Enterprise' mincer before digestion.

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Peptic Digestion.—The following experiments were carried out with (a) 75 g. of raw fish, (b) 75 g. of raw fish after frying, (c) 75 g. of raw fish after boiling for 20 minutes and (d) 75 g. of raw fish after boiling for 10 minutes. 75 G. of the tissue were treated with 75 c.c. of distilled water and left in a refrigerator overnight. Nexed day the p_H of the medium was adjusted to 2·0 with the addition of hydrochloric acid and the flask kept in a thermostat at 40° for half an hour. 10 C.c. of a 10% pepsin solution (Merck's) were then added to the mixture and the mixture incubated for 3 hours. 10 C.c. of the mixture were withdrawn from time to time and added to 50 c.c. of 95% alcohol and titrated with $N/25$ alcoholic caustic potash solution by means of a micro-burette (Willstätter's method). Each time a blank experiment was made by just adding the enzyme to the substrate and titrating immediately. Results are given in Table I.

TABLE I.

Digestibility of fish protein with pepsin.

Bengali name.	Zoological name.	Time of digestion.	No. of c.c. of N/25 alcoholic KOH.			
			Raw.	Fried.	Cooked.	Under-cooked.
			(a)	(b)	(c)	(d)
Rohu	*Labeo rohita*	60 min.	0·76	0·68	0·77	1·20
		120	1·40	0·82	0·92	1·45
		180	1·56	1·20	1·32	1·63
Hilsha	*Clupea ilisa*	60	1·30	0·86	0·96	1·28
		120	1·65	1·21	1·35	1·68
		180	1·72	1·52	1·62	1·84
Shinghi	*Saccobranchus fossilis*	60	1·25	0·92	0·88	1·31
		120	1.69	1·05	1·23	1 70
		180	1·88	1·34	1·45	1·92
Koi	*Anabas testudineus*	60	1·30	0·98	1·25	1·45
		120	1.62	1·25	1·38	1·52
		180	1·72	1·45	1·52	1 83
Mrigal	*Cirrhina mrigala*	60	0·82	0.73	0·81	0·96
		120	1·20	0·88	1·15	1 21
		180	1·49	1·16	1·35	1·43
Kalbasu	*Labeo calbasu*	60	0·82	0·73	0·81	0·96
		120	1·20	0.88	1·15	1 21
		180	1·49	1·16	1·35	1·52
Tengra	—	60	0·92	0·72	0·75	0·73
		120	1·10	0·96	0·96	1·10
		180	1·35	1·28	1·32	1·65
Parshey	*Mugil parsia*	60	1·10	0·82	1·12	1·21
		120	1·30	1·25	1.26	1·36
		180	1·73	1·55	1·63	1 80
Boal	*Wallago attu*	60	0·66	0·55	0·62	0·78
		120	0.89	0·78	0·91	0·96
		180	1·30	0·97	1·21	1·38
Shole	*Ophcephalus striatus*	60	0·95	0·75	0·72	1·15
		120	1·20	1·20	1·01	1·16
		180	1·63	1·50	1·52	1·2

Tryptic Digestion.—In these experiments 10 c.c. of a 10% solution of activated trypsin were added to 75 g. of the minced tissue (which had been heated with 75 c.c. of distilled water at 40° for half an hour) after adjusting the p_H of the medium to 8·5 by means of caustic potash solution. The determination of tryptic hydrolysis was carried out in the same way as in peptic digestion. In these experiments also a preliminary blank experiment was carried out in each case. Results are given in Table II.

The trypsin used was activated by means of cystine in the following way before use: 10 G. of trypsin (Merck) were placed in a 100 c.c. measuring flask with 50 c.c. of water, 5 c.c. of phosphate buffer $(M/15)$ at p_H 8·5

TABLE II.

Digestibility of fish protein with activated trypsin.

Bengali name.	Zoological name.	Time of digestion	No. of c.c. of $N/25$ alcoholic KOH.			
			Raw. (a)	Fried. (b)	Cooked. (c)	Under-cooked. (d)
Rohu	*Labeo rohita*	60 minute	0·54	0·53	0·62	1·00
		120	0·96	0·82	0·77	1·21
		180	1·23	1·03	1·28	1·35
Hilsha	*Clupea ilisa*	60	1·20	0·72	0·83	1·20
		120	1·42	1·11	1·25	1·53
		180	1·53	1·50	1·58	1·62
Shinghi	*Saccobranchus fossilis*	60	1·20	0·92	0·82	1·25
		120	1·42	1·15	1·20	1·53
		180	1·63	1·30	1·44	1·68
Koi	*Anabas testudineus*	60	1·10	0·88	0·82	1·12
		120	1·26	1·01	1·25	1·23
		180	1·52	1·43	1·48	1·64
Mrigal	*Cirrhina mrigala*	60	0·65	0·62	0·63	0·74
		120	0·83	0·78	0·92	1·20
		180	1·36	1·25	1·32	1·42
Kalbasu	*Labeo calbasu*	60	0·53	0·50	0·63	0·66
		120	0·84	0·73	0·79	0·96
		180	1·20	1·06	1·16	1·42
Tengra	—	60	0·83	0·66	0·70	0·84
		120	1·02	0·96	0·86	1·12
		180	1·25	1·17	1·29	1·63
Parshey	*Mugil parsia*	60	0·84	0·62	0·91	1·12
		120	1·02	0·73	1·20	1·31
		180	1·25	1·20	1·33	1·45
Boal	*Wallago attu*	60	1·25	1·10	1·26	1·20
		120	1·39	1·28	1·42	1·58
		180	1·52	1·48	1·56	1·63
Shole	*Ophcephalus striatus*	60	1·01	0·86	0·88	1·21
		120	1·26	1·20	1·36	1·38
		180	1·73	1·43	1·81	1·88

TABLE III.

Digestibility of fish protein with pepsin and trypsin.

Bengali name.	Zoological name.	Time of digestion.	No. of c c. of $N/25$ alcoholic KOH			
			Raw. (a)	Fried (b)	Cooked. (c)	Under-cooked. (d)
Rohu	Labeo rohita	60 min.	1·20	1·13	1·25	1·36
		120	1·82	1·46	1·53	1·92
Hilsha	Clupea ilisa	60	1·52	1·10	1·00	1·21
		120	1·65	1·32	1·43	1·82
Shinghi	Saccobranchus fossilis	60	1·33	1·21	1·30	1·52
		120	1·78	1·43	1·63	1·84
Koi	Anabas testu-dineus	60	1·52	1·22	1·38	1·61
		120	1·82	1·52	1·76	1·86
Mrigal	Cirrhina mrigala	60	1·20	0·92	1·21	1 31
		120	1·55	1·32	1·43	1·78
Kalbasu	Labeo calbasu	60	1·21	0·89	1·15	1·41
		120	1·53	1·28	1·48	1·63
Tengra	—	60	1·62	1·38	1·52	1·73
		120	1·85	1·45	1·68	1·93
Parshey	Mugil parsia	60	1·21	1·12	1·22	1·36
		120	1·65	1·42	1·53	1·68
Boal	Wallago attu	60	0·92	0·82	0·76	1·35
		120	1·46	1·20	1·36	1·72
Shole	Ophrephalus striatus	60	1·22	1·10	0·99	1·33
		120	1·69	1·28	1·43	1·96

and 5 c c. of 0·005M cystine solution at p_H 8·5 (Grassmann, *Z. physiol. Chem.*, 1930, **186**, 183). The flask was then kept in a thermostat for 30 minutes at 40°. The volume of the solution was made upto 100 c.c. with the addition of water heated to 40°.

Combined Action of Pepsin and Trypsin.—Fish (75 g. raw or after treatment) was treated with 75 c.c. of distilled water and the p_H of the mixture adjusted to 2·0 with hydrochloric acid. Pepsin (10%, 10 c.c.) was added in each of the flasks, which were incubated for 3 hours at 40°. The mixtures were then neutralised with caustic potash solution and the p_H was adjusted to 8·5 and treated with activated trypsin as described above. Results are shown in Table III.

DISCUSSION.

From the foregoing results it appears that the rate of digestion varies from species to species, which is apparently connected with differences in the

composition of the proteins of the fish. The rate of digestion of fish under-cooked in boiling water is greater than that of raw, fried or thoroughly cooked fish. This may be due to possible destruction of anti-enzymic properties in the under-cooked fish, while the proteins at this stage are not markedly denatured, which might have hindered the rate of hydrolysis. These findings are in agreement with those of Clifford (*Biochem. J.*, 1930 **24**, 1729) who states that overcooked meat is very slowly digested as compared with underdone meat and the maximum rate of digestion is obtained with the latter. With all the species under investigation the rate of hydrolysis is found to be greater in peptic digestion than in the tryptic except in the cases of Boal (*Wallage attu*) and Shole (*Ophcephalus striatus* where the results are reversed. When peptic digestion is followed by tryptic digestion hydrolysis is more complete than in the case of pepsin or trypsin alone. The results would indicate that in the normal process of digestion *in vivo*, the break-down of fish proteins would be fairly complete. But, as indicated above, in general the digestibility is the greatest with underdone fish as compared with raw, fully cooked or fried fish. In the case of the last two, digestibility is obviously impaired by denaturation, hardening and drying of the proteins.

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o-ALDEHYDO-CARBOXYLIC ACIDS. PART III. A SYNTHESIS OF 4:5 METHYLENEDIOXYPHTHALALDEHYDIC ACID AND NEW SYNTHESES OF 4- AND 5-METHOXY-PHTHALALDEHYDIC ACIDS.

By Satyendra Nath Chakravarti, Mahadevan Swaminathan and
P. R. Venkataraman.

4:5-Methylenedioxyphthaladeydic acid (V), for the synthesis of which an unsuccessful attempt was made by Stevens and Robertson (*J. Chem. Soc.*, 1927 2791) has been synthesised by us by methods similar to those employed in the case of the opianic acids (Chakravarti and Swaminathan, *J. Indian Chem. Soc.*, 1934, **11**, 715, 873).

4:5-Methylenedioxyhomophthalic acid (I), prepared by the hydrolysis of 4:5-methylenedioxy-2-carboxyphenylacetonitrile (Edwards, *J. Chem. Soc.*, 1926, 817) has been oxidised in boiling xylene solution by means of selenium dioxide to 4:5-methylenedioxyphthalonic acid (II), which is isolated as its aniline salt (III), which is then transformed to anilino-4:5-methylenedioxy-phthalaldehydic acid (IV) by boiling in dry xylene and which in its turn is hydrolysed to 4:5-methylenedioxyphthalaldehydic acid, m. p. 167°.

4:5-Methylenedioxyphthalaldehydic acid (V) gives on reduction with sodium amalgam 4 : 5-methylenedioxyphthalide (VII), which is also obtained by decarboxylating 4 · 5-methylenedioxyphthalide carboxylic acid (VI), obtained by the reduction of 4 : 5-methylenedioxyphthalonic acid (II) by means of sodium amalgam.

5 Methoxyphthalaldehydic acid (X) has been synthesised in the following manner. 2-Methyl-4-methoxyacetophenone (VIII) (*cf.* Noller and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1893) is oxidised by means of potassium permanganate to 5-methoxyphthalonic acid (IX), which in its turn is converted into 5-methoxyphthalaldehydic acid (X) *via* the sodium bisulphite compound.

COMe   CO·COOH   CHO
  ⬡Me   →   ⬡COOH   →   ⬡COOH
OMe   OMe   OMe
(VIII)   (IX)   (X)

When 2:6-dimethoxynaphthalene is oxidised, 5-methoxyphthalonic acid (IX) is found as the main product and 4-methoxyphthalonic acid (XII) is formed only in minute quantities (Chakravarti, *J. Indian Chem. Soc.*, 1933, **10**, 695). It was, therefore, thought that it may be possible to obtain 4-methoxyphthalonic acid in better yields by the oxidation of 2:7-dimethoxynaphthalene. On the oxidation of 2:7-dimethoxynaphthalene (XI), a mixture of methoxyphthalonic acids was obtained which is converted into the corresponding methoxyphthalaldehydo acids through the bisulphite compound.

MeO⬡CO·COOH   MeO⬡CHO
     COOH   →   COOH
      (XII)   (XIII)

MeO⬡⬡OMe

(XI)

MeO⬡COOH   MeO⬡COOH
     CO·COOH   →   CHO
      (IX)   (X)

It has been observed that 4-methoxyphthalaldehydic acid (XIII), m. p. 141°, is more soluble in water and much less soluble in benzene than

5-methoxy-acid (X), m. p. 144°, and this property has been utilised for separating the two isomers in a state of purity by a careful series of fractional crystallisations from benzene and water. The constitutions of these acids (XIII) and (X), (m. p. 141° and 144° respectively), obtained from the oxidation products, are established by direct comparison with authentic specimens, synthesised by methods which leave little doubt as to their constitution (Chakravarti, *loc. cit.* p. 697; Chakravarti and Swaminathan, *loc. cit.* p. 875).

An account of the synthesis of the remaining methoxy- and methylene-dioxy-*o*-aldehydocarboxylic acids is reserved for a future communication.

E X P E R I M E N T A L.

Aniline Salt of 4:5-*Methylenedioxyphthalonic Acid* (III).—4:5-Methylene-dioxyhomophthalic acid (5 g.) was suspended in dry xylene (400 c.c.) and the mixture heated to boiling. To the boiling mixture, selenium dioxide (3·3 g.) was added and the boiling continued for 3 hours, when the homophthalic acid gradually went into solution and a deep red solution containing a black deposit of selenium was obtained. The mixture was thoroughly extracted with dilute sodium carbonate solution and the combined extracts just acidified and evaporated to dryness. The residue was then taken up in boiling water (60 c.c.), filtered from a little insoluble residue and the filtrate treated with aniline (4 c. c.). The mixture was heated for ½ hour on the water-bath when the aniline derivative of 4:5-methylenedioxyphthalonic acid (III) separated (4 g.) The aniline derivative crystallised from alcohol in plates, m. p. 190°.

The p-*toluidine* derivative, prepared in a similar manner, crystallised from ethyl alcohol in leaflets, m. p. 193°. (Found: C, 66·6 ; H, 5·3. $C_{24}H_{22}O_6N_2$ requires C, 66·4; H, 5·1 per cent).

*Anilino-*4:5-*methylenedioxyphthalaldehydic Acid* (IV).—The aniline salt (2 g.) · was suspended in dry xylene (20 c. c.) and the mixture refluxed for 1½ hours, when a clear solution resulted. On cooling, the aniline derivative of 4:5-methylenedioxyphthalaldehydic acid separated, which after repeated crystallisation from alcohol was obtained as colourless plates, m. p. 187°. (Found . C, 66·6 ; H, 4·0. $C_{15}H_{11}O_4N$ requires C, 66·9; H, 4·1 per cent).

4:5-*Methylenedioxyphthalaldehydic Acid* (V).—The aniline derivative (IV) (1·5 g.) was heated with dilute hydrochloric acid (10 c.c.) on the steam-bath for 1½ hours. On cooling an acid separated in clusters of needles which, after recrystallisation from water and drying at 100°, melted at

167°.. It is readily soluble in alcohol, moderately soluble in benzene and practically insoluble in petroleum ether. (Found: C, 55·5 ; H, 3·1 $C_9H_6O_5$ requires C, 55·7; H, 3·1 per cent).

4:5-*Methylenedioxyphthalide-carboxylic Acid* (VI).—The compound (I) (5 g.) was oxidised under the conditions described above and the solution of the crude phthalonic acid in water (50 c. c.) was reduced by the gradual addition of sodium amalgam (100 g., 4%). The filtered solution was acidified, when the acid (VI) separated in clusters of shining needles, m. p. 223°, yield 2 g. It was recrystallised from water. (Found C, 53·9 ; H, 3·0. $C_{10}H_6O_6$ requires C, 54·1 ; H, 2·7 per cent).

4:5-*Methylenedioxyphthalide* (VII).—The acid (V) (0·3 g.), dissolved in dilute sodium hydroxide solution (5%, 10 c.c.), was reduced with excess of sodium amalgam (4%, 10 g.). The aqueous solution separated from the mercury, was filtered and acidified strongly and heated on the steam-bath for 15 minutes, when, on cooling, the phthalide separated in almost theoretical yield as prismatic needles, m p. 189° after crystallisation from water. It is sparingly soluble in benzene and almost insoluble in petroleum ether. It dissolves readily in methyl and ethyl alcohols.. The phthalide was also obtained by decarboxylating acid (VI) in boiling quinoline solution with copper chromite as a catalyst. The mixed m.p. of the specimens, obtained by the two methods, remained undepressed. (Found: C, 60·5; H, 3·6. $C_9H_6O_4$ requires C, 60·6; H, 3·4 per cent).

5-*Methoxyphthalaldehydic Acid* (X).—To a mixture of 2-methyl-4-methoxyacetophenone (VIII) (24 g.) and potassium carbonate (12 g. in 240 c. c. water) heated on the steam-bath, a hot solution of potassium permanganate (90 g. in 900 c. c. water) was gradually added with stirring. After the addition of all the permanganate, the whole was further heated for ½ hour on the steam-bath and filtered. The filtrate and the washings of the manganese precipitate were made just acid with hydrochloric acid and concentrated to a small volume. The hot liquid was then made alkaline with ammonia and treated with a concentrated solution of calcium chloride (48 g.) in water. The precipitated calcium salt (25 g.) was filtered, washed with water and then suspended in water. The mixture was heated to boiling, acidified with hydrochloric acid and the resulting solution cooled and extracted with ether (5 times). The ethereal extract was dried over sodium sulphate and the solvent removed. The residue was neutralised with dilute solution of sodium carbonate and evaporated to dryness. Freshly prepared sodium hydrogen sulphite solution (75 c.c. of 15%) was added to the salt and the whole evaporated to dryness on the steam-bath. The residue was further heated for one

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hour at 120° in an air-oven and then twice stirred up with excess. of hydrochloric acid and evaporated to dryness on the steam-bath in an open dish. This residue was then extracted twice with boiling benzene and the combined benzene extract concentrated to a small volume and allowed to remain when the acid (X) gradually separated (8 g.). It crystallised from water in beautiful silky needles, m. p. 144°. (Found: C, 59.8; H, 4.7. $C_9H_8O_4$ requires C, 60.0 ; H, 4.4 per cent).

Oxidation of 2:7-dimethoxynaphthalene (XI).—2:7-Dimethoxynaphthalene (prepared by methylation of 2 : 7-dihydroxynaphthalene with dimethyl sulphate in alkaline solution) was oxidised and the product of oxidation (a mixture of phthalonic acids) converted into the corresponding phthalaldehydic acids, under conditions similar to those described for 2:6-dimethoxynaphthalene (*cf.* Chakravarti, *loc. cit.*). The final benzene extract on cooling deposited crude 4-methoxyphthalaldehydic acid contaminated with some 5-methoxyphthalaldehydic acid (A). The whole was filtered and the residue (A) was twice crystallised from benzene and then from water when 4-methoxy acid (XIII) separated in balls of minute prismatic needles, m.p. 141°. (Found : C, 59.9 ; H, 4.6. Calc. for $C_9H_8O_4$: C, 60.0 ; H, 4.4 per cent). A mixed melting point with 4-methoxyphthalaldehydic acid previously synthesised (Chakravarti and Swaminathan *loc. cit.*) caused no depression.

The benzene mother-liquors from (A) were concentrated to a very small volume and the solid which separated was repeatedly crystallised from hot water when 5-methoxyphthalaldehydic acid (X) was obtained in beautiful long needles, m. p. 144°. (mixed m. p. with an authentic specimen previously synthesised, Chakravarti, *loc. cit.*). (Found : C, 59.8 ; H, 4.5. Calc. for $C_9H_8O_4$: C, 60.0 ; H, 4.4 per cent).

Pure 4-methoxyphthalaldehydic acid (XIII) is sparingly soluble in benzene and very easily soluble in water, while 5-methoxy acid (X) is much more soluble in benzene and less soluble in water.

During the oxidations considerable quantities of 2:7-dimethoxynaphthalene were recovered unchanged (8 g. from 20 g.) by extracting the precipitated manganese dioxide etc. with boiling acetone. This shows that probably better yields of the oxidation products could be obtained by oxidising the corresponding hydroxymethoxynaphthalenes. This point is being investigated.

Part of the work recorded in this paper was done at Annamalainagar during 1935-1936.

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CHEMICAL EXAMINATION OF *BLEPHARIS EDULIS*, PERS. PART III. CONSTITUTION OF BLEPHARIN.

By Jagraj Behari Lal.

Blepharin, $C_{16}H_{20}O_{10}$, m.p. 222°, is an optically active β-glucoside, containing 5 hydroxyl groups and gives on acid hydrolysis the aglucone, m.p. 178°.

In Part I of this series of communications (*J. Indian Chem. Soc.*, 1936, **13**, 109) the author has recorded the isolation of a crystalline bitter glucoside, *blepharin* (m.p. 222°) in addition to a colourless nitrogenous compound, identified as allantoin. Blepharin crystallises in beautiful shining colourless crystals from alcohol, acetone or water, either in the form of long rectangular plates or rhombic prisms.

It has the molecular formula $C_{16}H_{20}O_{10}$. The air-dried crystals of blepharin as obtained from rectified spirit and moist acetone have the composition $C_{16}H_{20}O_{10}$, $1\frac{1}{2}$ H_2O. It is a β-glucoside and is optically active.

Anhydrous blepharin does not contain any methoxyl or ethoxyl group, but contains five alcoholic hydroxyl groups, as it forms a pentacetyl derivative, silky needles, m.p. 183'; pentacarbethoxy derivative, silky needles, m.p. 191° after shrinking at 185°; and a penta-*p*-nitro-benzoyl derivative, m.p. 264° after shrinking at 258°. Blepharin is saturated and does not contain any ethylenic double bond. On bromination in chloroform it chars and crystalline derivatives cannot be isolated. In blepharin aldehydic or ketonic groups are absent, as it neither gives any colouration with Schiff's reagent nor does it react with hydroxylamine, phenyl semicarbazide or phenylhydrazine. On hydrolysis with dilute hydrochloric acid it gives the aglucone as stout prismatic needles, m.p. 178°, which is being further investigated.

Experimental.

Blepharin is optically active, a sample crystallised from alcohol having $[\alpha]_D^{31\cdot5}, +121\cdot5°$ (*c*, 0·7676). It is hydrolysed by emulsin at room temperature (30°) and is therefore a β-glucoside. [Found in air-dried sample from water: C, 47·97, 48·04; H, 5·61, 5·73; loss at 120°, 7·20. (micro) C, 47·91, 47·85; H, 5·58, 5·66; loss in vacuum at 100° (micro), 6·36, 7·10. $C_{16}H_{20}O_{10}$, $1\frac{1}{2}$ H_2O

requires C, 48·12; H, 5·76; loss, 6·77 per cent]. [Found in sample dried
in high vacuum at 100° (micro): C, 51·24, 51·32; H, 5·34, 5·40. Found in
sample dried at 120°: C, 51·47; H, 5·42; M.W. in water (ebulioscopic), 360,
392; M.W. in phenol (cryoscopic), 360, 330. $C_{16}H_{20}O_{10}$ requires C, 51·62;
H, 5·38; M.W., 372. Found in air-dried sample from alcohol: C, 48·24,
48·05; H, 5·44, 5·60; loss at 120°, 6·99. $C_{16}H_{20}O_{10}$, $1\frac{1}{2}$ H_2O requires C, 48·12;
H, 5·76; loss, 6·77 per cent. Found in sample from alcohol dried at 120°: C,
51·48; H, 5·42. Found in air-dried sample from moist acetone: C, 48·85,
49·08; H, 5·50, 5·63; loss at 120°, 5·44. $C_{16}H_{20}O_{10}$, H_2O requires C, 49·22; H,
5·64; loss 4·62 per cent].

Carbethoxyblepharin was prepared by adding ethyl chlorocarbonate
(13 g.) drop by drop to a solution of blepharin (1·8 g.) in pyridine (30 c.c.)
and cooling the mixture in tap water. After 3 hours the product was
poured into water when an oily mass separated which was washed with water
and on standing overnight under water solidified and crumbled to a fine
powder. It was filtered, well washed and dried in air. After two crys-
tallisations from boiling alcohol it was obtained as beautiful, large silky
needles, m.p. 161·5°. It is insoluble in boiling water, ether and petroleum
ether, and is very soluble in cold pyridine, chloroform and carbon tetra-
chloride. It is fairly soluble in cold ethyl and methyl alcohol. It is
very slightly soluble in cold acetone, ethyl acetate, amyl alcohol,
benzene and more in the boiling solvents. [Found: C, 50·70, 50·72; H,
5·42, 5·50; loss at 125°, 0·23; M.W. of sample dried at 120° (ebulioscopic) in
ethyl alcohol, 708, 729. $C_{16}H_{15}O_{10}$ $(COOC_2H_5)_5$ requires C, 50·81; H, 5·46
per cent. M. W., 732].

Acetylblepharin.—A mixture of blepharin (2 g.), anhydrous sodium
acetate (2 g.) and acetic anhydride (17 g.) was heated under reflux at 120°
for 5 hours and the cooled mixture was poured into a large volume of water;
on keeping silky needles separated which were filtered, washed and dried in
air, m.p. 167-168° after shrinking at 151°, yield 1·95 g. The product after
two crystallisations from small quantities of ethyl alcohol was finally crystal-
lised from hot dilute alcohol as tiny glistening needles, m.p. 183°. It is very
soluble in cold alcohol, acetone, ethyl acetate, pyridine, chloroform and very
slightly in benzene, amyl alcohol, ether and petroleum ether. [Found in
air-dried sample: C, 53·35, 53·40; H, 5·10, 5·14; CH_3CO, 36·4, 36·7; loss
at 120°, 0·42; M.W. in ethyl alcohol (ebulioscopic), 581, 552. $C_{16}H_{15}O_{10}$
$(CO CH_3)_5$ requires C, 53·61, H, 5·16; CH_3CO, 36·88; M.W., 581].

p-Nitrobenzoylblepharin.—To blepharin (1·6 g.), dissolved in pyridine
(30 g.), finely powdered *p*-nitrobenzoyl chloride (10 g.) was added with
vigorous shaking during the course of 3 hours. The mixture after

standing overnight was treated with excess of water when a viscous liquid separated, which on treatment with a solution of sodium bicarbonate became solid and crumbled to a fine white powder. It was filtered, washed repeatedly with water, dried in air, m.p. $254°$ after shrinking at $258°$, yield 4.5 g. It is almost insoluble in water, hot ethyl and methyl alcohol, acetone, ethyl acetate, chloroform, benzene, ether and petroleum ether but extremely soluble even in pyridine and fairly in hot dilute pyridine. On crystallisation from hot dilute pyridine after washing with water and drying in air the crystals melted at $264°$ after shrinking at $258°$. It did not suffer any loss on drying in an air-oven at $125°$ for 12 hours or on heating at $110°$ in high vacuum over calcium chloride. [Found: C, 54.58; H, 3.29; N $6.3, 6.5$. $C_{18}H_{15}O_5 (C_7H_4NO_4)_5$ requires C, 54.8; H, 3.14; N, 6.3 per cent).

O-*Methylblepharin* was obtained in poor yield by methylating blepharin (2 g.) in alkaline solution with methyl sulphate (30 g.) in the usual manner. It melted at $130°$ (decomp.) after shrinking at $128°$.

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THE CONSTITUENTS OF ALKANET ROOT (*ANCHUSA TINCTORIA*, LAM) PART II. ANCHUSIN AND ITS DERIVATIVES.

BY D. N. MAJUMDAR AND (LATE) G. C. CHAKRAVARTY.

A new colouring matter, anchusin ($C_{30}H_{36}O_9$), has been isolated from alkanet root. Anchusin is probably an anthraquinone derivative containing three hydroxyl groups, two of which are phenolic. β-Methylanthracene has been isolated by the distillation of anchusin with zinc dust under reduced pressure. The oxidation and bromination of anchusin have also been studied.

While the controversies regarding the constitution of alkannin, one of the colouring matters of alkanet, were going on (Betrabet and Chakravarty, *J. Indian Inst. Sci.*, 1933, **16A**, 41) we thought it desirable to search for other colouring matters in the alkanet root as it is usually found that a naturally occurring compound is invariably associated with other compounds of the same type.

Gawalewski (*Chem. Zentrl.* 1902, **II**, 1001) found that the alkanet roots contain also two colouring matters, anchusic acid ($C_{30}H_{39}O_7$) and alkanic acid ($C_{30}H_{28}O_8$) and Erikson (*Ber. Deut. Pharm. Ges.*, 1910, **20**, 202) observed that of the two pigments one gives blue and another green solution with alkalis.

Anchusin has been obtained from the residue of the powdered alkanet root after extraction with petroleum ether. It is purified by precipitating the chloroform solution with benzene in which alkannin is very soluble whereas anchusin is very sparingly soluble. The precipitated anchusin is finally crystallised from alcohol in dark red micro-crystalline powder. The analytical results of anchusin and the analyses of the potassium derivative and the barium compound show that the molecular formula of anchusin is $(C_{10}H_{12}O_3)_3$. On acetylation a triacetylanchusin and tetra-acetyleuco-anchusin are obtained. Benzoylation gives a tribenzoyl derivative. The results indicate the presence of three hydroxyl groups in anchusin molecule and also an easily reducible carbonyl group. Methylation of anchusin gives a dimethoxy derivative which on further acetylation gives a dimethoxy-acetyl derivative showing thereby that two of the three hydroxyl groups are phenolic in character.

When distilled with zinc dust under high vacuum anchusin yields a small quantity of methylanthracene together with a yellow oil of peculiar smell. Anchusin thus appears to be an anthracene derivative.

On oxidation with 2N-nitric acid anchusin yields four different nitrogen-containing carboxylic acids of high-melting-points and oxalic acid. The yields of the acids are not sufficient for their identification.

It thus appears that alkannin and anchusin possess molecular complexity of the same order and the latter may be more saturated than the former. Moreover, it has been observed that on oxidation of alkannin with 2 N-nitric acid under similar-condition it also gives a mixture of nitrogen-containing carboxylic acids of similar complexity. In spite of their non-identification it may be presumed that there is a good deal of similarity between these two colouring matters and both are derivatives of anthraquinone.

From the residue left after the extraction of anchusin, a third colouring matter has been isolated with chloroform which is insoluble in ether and benzene but soluble in chloroform. It gives indigo-blue solution with caustic soda and potash. We propose to designate it as 'Tinctorin' instead of alkananin, (*Proc. Ind. Sci. Congress*, 1933. p. 206). Further work is in progress.

Experimental.

Isolation of Anchusin.—The powdered root bark (20 lbs) was extracted first with petroleum ether (50-60°) to remove alkannin and wax in a modified Soxhlet apparatus (Sando, *Ind. Eng. Chem.*, 1924, **16**, 1125) till the final extract was colourless. The residues, left after extraction, were freed from the solvent and the dry powder was again extracted with ether in the same apparatus. The ethereal extract was freed from the solvent and a dark red amorphous and brittle product was obtained (8% of the root bark). It was digested with boiling benzene and the insoluble residue was dissolved in chloroform and precipitated with benzene. The process was repeated twice. Anchusin, thus obtained, was further purified by crystallisation from alcohol when it was obtained as a dark red micro-crystalline powder, decomposing above 300° with evolution of brown fumes after shrinkage at 185°. It is soluble in alcohol, acetone, acetic acid, pyridine, chloroform and sparingly soluble in benzene and ether and insoluble in petroleum ether. It can be precipitated from its green alkaline solution with acid. (Found : C, 66·8; H, 6·7. $C_{30}H_{36}O_9$ requires C, 66·67 ; H, 6·67 per cent).

The *barium salt* was prepared from alcoholic solution of anchusin (5 g) with an ammoniacal solution of barium chloride. The greenish precipitate was filtered and washed thoroughly with water, alcohol and ether. [Found : Ba, 12 7. $(C_{30}H_{35}O_9)_2$ Ba requires Ba, 11·3 per cent].

The *potassium salt* was obtained by treating an alcoholic solution of anchusin (5 g.) with an excess of alcoholic potash and the green precipitate was washed with alcohol and ether. (Found: K, 12·16. $C_{30}H_{34}O_9K$ requires K, 12·68 per cent).

Barium Potassium Compound.—An aqueous solution of the potassium salt of anchusin (5 g.) was mixed with barium chloride solution. The precipitate was washed with hot water till free from potassium chloride. [Found: Ba, 10·98. $(C_{30}H_{34}O_9 K)_2$ Ba requires Ba, 10·64 per cent].

Triacetylanchusin.—Anchusin (50 g.), fused sodium acetate (100 g.) and an excess of acetic anhydride were heated under reflux for 5 hours at 130-40°. The crude acetyl derivative was washed with dilute alkali and then with water and the dry compound was again washed with boiling absolute alcohol several times to remove last traces of anchusin. The residue was dissolved in ethyl acetate and precipitated with absolute alcohol. It was crystallised from glacial acetic acid in microcrystalline powder, decomposing at 212-15° with shrinkage at 175-76°. [Found : C, 65·2 ; H, 6·05 ; $COCH_3$, 19·3; M.W. (Walker, Lumsden and Mc.Coy, *J. Amer. Chem. Soc.*, 1900, **23**, 353), 634·6. $C_{30}H_{33}O_9(COCH_3)_3$ requires C, 64·86 ; H, 6·3 ; $COCH_3$, 19·3 per cent. M.W. 666).

Tetraacetyl-leuco-*anchusin.*—A mixture of anchusin (15 g.), acetic anhydride (300 c.c.), zinc dust (45 g.) and fused sodium acetate (45 g.) was heated under reflux for 5 hours at 130-40°. After cooling the filtered deep yellow solution was poured into an excess of water and the yellow precipitate was collected and washed with dilute alkali and water. It was dissolved in ethyl acetate and precipitated with petroleum ether and washed with boiling absolute alcohol. The residue crystallised from glacial acetic acid in deep yellow crystalline powder, m.p. 210° (decomp.) shrinking at 190-91°. [Found : C, 65·4 ; H, 6·1 ; $COCH_3$, 24·77. $C_{30}H_{34}O_9 (COCH_3)_4$ requires C, 64·3 ; H, 6·4 ; $COCH_3$, 24·3 per cent]

Dimethoxyanchusin was prepared from an alkaline solution of anchusin with dimethyl sulphate. The crude product was dissolved in chloroform and precipitated with petroleum ether and the precipitate digested with absolute alcohol and the residue crystallised from glacial acetic acid as microcrystalline powder, m.p. 240-42° (decomp.). It is a dark brownish powder, insoluble in benzene, petroleum ether and alcohol but soluble in acetone, chloroform, pyridine and ethyl acetate. [Found : C, 67·4 ; H, 6·9 ; OMe, 10·5. $C_{30}H_{34}O_7 (OMe)_2$ requires C, 67·6 ; H, 7·0; OMe, 10·9 per cent].

Dimethoxyacetylanchusin.—Methoxyanchusin (5 g.) was acetylated as before and the product was extracted with benzene and precipitated with

petroleum ether. It was crystallised from glacial acetic acid in brown crystalline powder, not melting up to 330°. It is soluble in benzene, chloroform, ethyl acetate, pyridine, glacial acetic acid but insoluble in methyl and ethyl alcohol and petroleum ether. [Found : C, 67·3, H, 6·5; COCH₃, 7·4 ; OMe, 9·8. $C_{30}H_{33}O_7$ $(OMe)_2$ $COCH_3$ requires C, 66·9 ; H, 6·9 ; COCH₃, 7·0; OMe 10·10 per cent].

Tribenzoylanchusin was prepared from anchusin (5 g.) in pyridine solution with benzoyl chloride. The crude product was dissolved in acetone, dehydrated with sodium sulphate and the residue, after the removal of the solvent, was dissolved in benzene and precipitated with petroleum ether. It was finally digested with absolute alcohol and the residue precipitated from benzene with petrol as brown powder, m.p. 226-28° (decomp.). [Found: C, 72·0 ; H, 5·5. $C_{30}H_{33}O_9$ $(COC_6H_5)_3$ requires C, 71·8; H, 5·63 per cent].

Bromination of Anchusin.—(ı) Finely powdered anchusin (3 g.) was placed on a watch-glass and kept in a desiccator with an excess of dry bromine. The solid was occasionally stirred. A sticky mass was obtained after 5 days and was freed from excess of bromine by evacuation. The dark brown powder, thus obtained, was crystallised from absolute alcohol in brick-red powder, decomposing with shrinkage at 248-50°. (Found: Br, 37·9. $C_{30}H_{32}O_9Br_4$ requires Br, 37·3 per cent). The residue from absolute alcohol was crystallised from glacial acetic acid in dark red microcrystalline powder, decomposing above 310°. (Found : Br, 47·4. $C_{30}H_{30}O_9Br_6$ requires Br, 47·3 per cent).

(*ii*) Anchusin (5 g.) was dissolved in glacial acetic acid (70 c.c.) and acetic acid solution of bromine (30 c.c.) was added gradually at 0° with constant stirring. The reaction mixture was slowly brought to the room temperature and heated on a water-bath for 2½ hours. The mixture after cooling was poured into an excess of cold water and the brick-red precipitate was collected, washed with water and dried over sulphuric acid under vacuum. It was crystallised from absolute alcohol in brick red powder, m.p. 160-65° (decomp.) (Found: C, 34·9 ; H, 3·09 ; Br, 47·4. $C_{30}H_{30}O_9Br_6$ requires C, 35·5 ; H, 2·96 ; Br, 47·3 per cent).

The residue from above was crystallised from glacial acetic acid in brick-red crystalline powder, m.p. above 310° (decomp.). (Found : Br, 48·2. $C_{30}H_{30}O_9Br_6$ requires Br, 47·3 per cent). The residue from glacial acetic acid was crystallised from acetone in dark brown microcrystalline powder, decomposing without melting above 260°.

(*iii*) The above experiment (*ii*) was repeated without heating at the end. The precipitate after drying was extracted with absolute alcohol when most of it went into solution leaving a very small dark amorphous mass which could not be analysed.

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The alcoholic solution gave a brick-red crystalline powder, decomposing above 270°. (Found : C, 41·7 ; H, 3·4 ; Br, 38·1. $C_{30}H_{32}O_9Br_4$ requires C, 42·0; H, 3·7 ; Br, 37·4 per cent).

Oxidation of Anchusin.—Finely powdered anchusin (20 g.) was heated to boiling for 5 hours with an excess of 2 N-nitric acid, and kept overnight. The insoluble residue (A) was filtered off from the brown solution (B).

The solution was concentrated to a small volume on a water-bath and finally evaporated to dryness in a desiccator over caustic potash and calcium chloride. The brown hygroscopic substance was digested with ether and the residue consisted of a colourless crystalline product and a fine brown powder. They were separated mechanically by stirring with ether. The brown highly hygroscopic powder containing nitrogen could not be crystallised from any solvent. The colourless crystalline powder was recrystallised from alcohol in needles, m.p. 99-100°. It was confirmed to be oxalic acid (*p*-toluidino-compound, m.p. 264-65°). The ethereal solution gave a further quantity of oxalic acid, m.p. 99-100° and a nitrogen-containing resinous substance which could not be identified.

The insoluble residue (A), when digested with hot water, left behind a small quantity of a solid which was crystallised from alcohol in yellowish orange crystalline powder, not melting up to 320°. It contains nitrogen and dissolves in sodium bicarbonate solution with evolution of carbon dioxide. The hot aqueous extract was evaporated nearly to dryness first in *vacuo* then over sulphuric acid in a desiccator. The orange powder, thus obtained, was extracted successively with ether, benzene and absolute alcohol. All these extracts gave high melting orange solids which vary from one another in their intensity of colour. They all contain nitrogen and dissolve in sodium bicarbonate solution with evolution of carbon dioxide.

Distillation of Anchusin with Zinc dust.—A mixture of anchusin with twice its weight of purified zinc dust was distilled under reduced pressure and the small amount of yellowish viscous oil, thus obtained, was dissolved in benzene and washed successively with caustic soda and water. The solution after dehydration with sodium sulphate gave a crystalline residue, which was recrystallised from alcohol in colourless plates, m.p. 199-200°. (mixed m.p. with a genuine sample of β-methylanthracene).

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A PRELIMINARY NOTE ON MESUOL, THE BITTER PRINCIPLE OF *MESUA FERREA*.

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and Prafulla Kumar Bose.

The bitter fatty oil of the seed kernel of *Mesua ferrea,* Linn. (N. O. *Guttiferea*), known in India as Nagkesar or Nageshwar oil, has been the subject of a number of investigations (Boorsma, *Bull. Inst. Botan. Buiten-zorg*, 1904, 21, 4 ; Hooper, *Pharm. J.*, 1908, 27, 161 ; Grimme, *Chem. Rev. Fett. Harzind.*, 1910, 17, 156 ; Dhingra and Hilditch, *J. Soc. Chem. Ind.*, 1931, 50, 9T ; Chatterjee and Gupta, *Oil Col. Trades J.*, 1937, 91, 1656). Very little is, however, known regarding the other constituents of the seeds. Boorsma (*loc. cit.*) reported the presence of two resinous bitter principles, but they did not receive further attention.

Chatterjee and Gupta (*loc. cit.*) observed that Nageshwar oil produces a deep yellow colour in contact with dilute aqueous alkali. This phenomenon is characteristic of the oil, and it must be due to some principle other than the normal constituents of a vegetable oil. It had moreover been observed by previous investigators that the expressed oil deposited a solid ' stearin ' on keeping. Microscopic examination of this deposit revealed the presence of a crystalline substance, which was found to dissolve in aqueous alkali with a deep yellow colour. Obviously the ' stearin ' is responsible for the production of the yellow alkali salt. We thought it desirable to examine the crystalline substance in greater detail. The want of a suitable hydraulic press led us to attempt its isolation from the oil extracted by means of solvents. The best results have been obtained by a method which is detailed in the Experimental. The pure compound, obtained in a yield of nearly 1%, formed pale yellow, transparent prisms, m.p. 154°. It is apparently different from the amorphous principles isolated by Boorsma. The name ' Mesuol ' is proposed for this substance which appears to be a new one.

Mesuol is neutral to litmus and has a slight bitter taste. It is soluble in 1% aqueous alkali, 10% ammonia and hot sodium carbonate solutions, but insoluble in sodium bicarbonate. Acids precipitate the compound unchanged from the deep yellow alkaline solutions. The colour with ferric chloride in alcohol medium is dirty olive-green. Mesuol is obviously phenolic in character. It is optically inactive, and is free from methoxy and

methylenedioxy groups. The yellow colour of mesuol in alcohol is deepened on the addition of lead acetate, but no precipitate is formed. Treatment with hydrochloric acid and metallic magnesium did not produce any colour. It is evidently not a hydroxyflavone. The analytical and M. W. data agreed with the formula, $C_{23}H_{22}O_5$ or $C_{22}H_{20}O_5$. The analytical values of dimethylmesuol, however, lend support to the former. We, therefore, tentatively assign the molecular formula, $C_{23}H_{22}O_5$, to mesuol.

The dimethyl derivative, just referred to, was obtained in quantitative yield by methylation of mesuol with methyl iodide in acetone medium in presence of potassium carbonate. Dimethylmesuol is indifferent fo ferric test, but showed the presence of lactone ring. Methylation with diazomethane does not proceed to complete methylation of the two phenolic OH groups of mesuol.

The elucidation of the structure of mesuol by further experiments which are in progress will form the subject of a future communication.

E X P E R I M E N T A L.

Isolation of Mesuol.—The seeds of *M. ferrea* were collected from the district of Sylhet in Assam. The kernels of the air-dried material were coarsely powdered and extracted with light petroleum (b.p. 40-50°) in a large Soxhlet during 18 hours. The reddish brown extract was freed from the major part of the solvent and allowed to stand at about 20° for several days. After three weeks the crystalline deposit of crude mesuol was collected and freed from adhering fat by washing with petroleum ether in which mesuol is almost insoluble. The product was then repeatedly crystallised from methyl alcohol, benzene-petroleum ether and dilute acetone in succession. The first crop of crystals from the last named solvent usually formed yellow, opaque, feathery crystals, m. p. 152°, which were rejected. Mesuol separated from dilute acetone as pale yellow, compact, transparent prisms, m.p. 154°. Further crystallisations failed to alter the m. p. Purified by distillation at 190-200°/0·04 mm. and subsequent crystallisation from methyl alcohol, it had the same m.p. [Found in samples dried at 110° in *vacuo* over P_2O_5 : C, 72·7, 72·7; H, 6·2, 6·02. M. W. (cryoscopic in benzene), 377, 378. $C_{22}H_{20}O_5$ requires C, 72·53 ; H, 5·5 per cent. M. W. 364. $C_{23}H_{22}O_5$ requires C, 73·03 ; H, 5·82 per cent. M.W., 378).

Mesuol is readily soluble in warm alcohol, acetone, benzene, chloroform and pyridine, moderately in carbon bisulphide and sparingly in ether. It dissolves in concentrated sulphuric acid with a greenish yellow colour. It is insoluble in concentrated hydrochloric acid.

Dimethylmesuol. — To mesuol (0·2 g.), dissolved in dry acetone (15 c.c.), were added methyl iodide (0·4 g.) and anhydrous potassium carbonate (0·5 g.). The mixture was refluxed on the water-bath for 5 hours. The orange-yellow colour of the solution faded to straw-yellow after completion of the reaction. The solution was freed from insoluble potassium salts and evaporated to dryness. The oily residue solidified on treatment with a little methyl alcohol in the cold. The crystals were collected, washed with water and recrystallised from methyl alcohol, m.p. 131°. Further purified by distillation in high vaccum (170-75°/0·04 mm.) and subsequent crystallisation from ligroin, it formed colourless prisms or plates, m.p. 132°. [Found in samples dried at 110° in *vacuo* over P_2O_5 : C, 73·7 ; H, 6·49 per cent. M.W. (cryoscopic in benzene), 407. $C_{25}H_{26}O_5$ requires C, 73·88 ; H, 6·4 per cent. M. W., 406).

Dimethylmesuol is soluble in most organic solvents but not in water. Its alcoholic solution turned deep yellow on the addition of 10% aqueous alkali, but the colour faded to pale apple-green on keeping or warming. Dilution of the alkaline solution did not give any precipitate. On adding mineral acids an oil separated out, which solidified on keeping overnight. Crystallised from methyl alcohol it melted at 132° alone or when mixed with dimethylmesuol. The solution in concentrated sulphuric acid is greenish yellow.

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A NOTE ON THE KEEPING PROPERTIES OF *HYDNO-CARPUS WIGHTIANA* OIL AND ITS DERIVATIVES.

By U. P. BASU AND A. MAZUMDAR.

It has been recently shown by us (*Leprosy in India*, 1939, **11**, 53) that the addition of creosote (4%), or hydroquinone (0·02%) inhibits the autooxidation and markedly improves the keeping properties of *Hydnocarpus Wightiana* oil as well as the iodized ethyl esters of the acids derived from this oil. This retarding effect of creosote has now been observed at still a lower concentration (0·1-0·2%'. The oil contains an unsaponifiable substance (about 0·02%), which is, however, not pro-oxygenic in nature.

A concentrate, prepared by a slight modification of the method of Green and Hilditch (*J. Soc. Chem. Ind.*, 1937, **56**, 23 T), from the oil cake of the *Hydnocarpus Wightiana*, dissolved in sodium bicarbonate, reduced Fehling's solutions and showed the presence of nitrogen and was insoluble in ether but possessed no appreciable anti-oxygenic power. A similar concentrate prepared from sesame oil cake, however, possessed a considerable antioxygenic activity. Thus, the peroxide value 63·8 (in terms of 0·01 N-thio.), obtained by heating an oil at 100° for about 4½ hours was reduced to about 2·6 when the oil was mixed with 0·5% concentrate from the latter cake. This concentrate is very rich in nitrogen (6·1%), and also insoluble in petrol ether. Further work in this direction is in progress.

A NEW FORMULA FOR CHAKSINE, THE ALKALOID OF *CASSIA ABSUS* AND SOME EXPERIMENTS ON ITS CONSTITUTION.

By Hans Raj Kapur, Kidar Nath Gaind, Kartar Singh Narang
AND Jnanendra Nath Ray.

The formula of chaksine, the alkaloid from *Cassia absus,* has been found to be $C_{11}H_{21}O_3N_3$ and not $C_{12}H_{21}O_2N_3$ as suggested by Siddiqui and Ahmed.

Siddiqui and Ahmed (*Proc. Indian Acad. Sci.*, 1935, **2A**, 421) have isolated two quaternary bases from the seeds of *Cassia absus*. The base chaksine has been given the formula $C_{12}H_{21}O_2N_3$ and its salts have been formulated as $C_{12}H_{20}ON_3Hal$. These authors isolated the iodide for which they found I, 39·4%, whilst their formula $C_{12}H_{20}ON_3I$ required I, 36·4%. Apart from this, they relied on the analysis of chaksine bicarbonate which was supposed to have the composition $C_{12}H_{20}ON_3.HCO_3, \frac{1}{2}H_2O$. It was dehydrated by heating at 100° and the anhydrous substance analysed. There is grave objection to accept the loss in *vacuo* at 100° to be due to the loss of $\frac{1}{2} H_2O$. It is quite well known that the bicarbonates of organic bases, like those of an alkali metal, lose carbon dioxide on heating as indeed has been found to be the case by us.

It appeared to the present authors that the formula of chaksine has not been satisfactorily determined. Chaksine iodide was prepared essentially by the method of Siddiqui and Ahmed (*loc. cit.*) but the substance had m.p. 180° with previous shrinkage (Siddiqui and Ahmed give m.p. 168°). We have also prepared the sulphate, nitrate, chloride and the bromide in a high state of purity and analysed these carefully. The results do not confirm the formula $C_{12}H_{20}ON_3X$. For example the iodide gives C, 37·2, 37·1 ; H, 6·1, 6·3 ; N, 11·9, 11·7 ; I, 34·9 (Siddiqui and Ahmed's data), whilst $C_{12}H_{20}ON_3I$ requires C, 41·2 ; H, 5·7 ; I, 36·4%, whereas $C_{11}H_{20}O_2N_3I$ requires C, 37·37 ; H, 5·7 ; N, 11·9 ; I, 35·9%. Siddiqui and Ahmed did not record any C and H values for the iodide.

Siddiqui and Ahmed have described the platinichloride of the chloride and from their data the M.W. for the chloride comes out as 261·5. The chloride itself has been prepared by us and analysed. It gives C, 50·57 ; H, 8·1 ; N, 15·5, 15·66. $C_{11}H_{20}O_2N_3Cl$ requires C, 50·48, H, 7·7 ; N, 16·0 ; M.W. 261·5, whilst $C_{12}H_{20}ON_3Cl$ requires C, 55·9 ; H; 7·7

N, 16.3%. Therefore it would appear that chaksine is $C_{11}H_{21}O_3N_3$, ($C_{11}H_{23}O_3N_3$ is also possible from the analytical data but less probable) and not $C_{12}H_{21}O_2N_3$ as suggested by Siddiqui and Ahmed. In the experimental sequel, we have described the preparation and analyses of a large number of salts which mitigate clearly against C_{12}-formula for chaksine.

The nitrate of chaksine gives with strong sulphuric acid a substance which we have designated as nitrochaksine sulphate formed by the loss of a molecule of water reminiscent of urea nitrate-nitrourea or guanidine nitrate—nitroguanidine change. With ·sodium hydroxide and barium hydroxide ammonia is copiously liberated from chaksine but unfortunately the product of the action of alkali has not yet been isolated in a state of purity. With hydrogen peroxide and trace of ferrous sulphate, chaksine sulphate gives formaldehyde recognised by the dimedon condensation product. With potassium permanganate, chaksine sulphate gives oxalic acid and a mixture of dibasic acids which have been separated by esterification and fractionation, of these esters one analysed as $C_{10}H_{18}O_4$, and another as $C_7H_{14}O_3$.

Further work is in progress.

EXPERIMENTAL.

In the extraction of chaksine from the seeds, ethyl alcohol was substituted for methyl alcohol prescribed by Siddiqui and Ahmed. The brownish yellow syrupy residue, after the removal of solvent at 40° from the neutralised and acidified extract, was freed of oily matter by repeated extraction with ether.

The *iodide*, isolated essentially as described by Siddiqui and Ahmed, was repeatedly crystallised from hot water, m.p. 180° (after drying in high *vacuo* at 100°). [Found: C, 37·1, 37·2; H, 6·3, 6·1; N, 11·9, 11·9, 11·7; (Siddiqui and Ahmed gave I, 34·9). Calc. for $C_{11}H_{20}O_2N_3I$: C, 37·3 ; H, 5·7 ; N, 11·9 ; I, 35·9 per cent].

Chaksine sulphate, prepared from chaksine iodide or as described by Siddiqui and Ahmed, was repeatedly crystallised from water or dilute alcohol, m.p. 317° (decomp.). [Found after drying in high *vacuo* at 140°: C, 48·0; H, 7·7; N, 15·0, 14·96; S, 5·55. $(C_{11}H_{20}O_2N_3)_2SO_4$ requires C, 48·18 ; H, 7·3 ; N, 15·3 ; S, 5·84 per cent. Siddiqui and Ahmed gave S, 5·85%. They do not give any other values. $(C_{12}H_{20}ON_3)_2SO_4$ requires C, 53·3 ; H, 7.4 ; N, 15.5 ; S, 5.93 per cent].

Chaksine Chloride.—To a hot suspension of chaksine sulphate in water (1 g. in 20 c.c.) was added powdered barium chloride (4 g.). After boiling

for 2 minutes, the solution was filtered and the filtrate saturated with sodium chloride. The crystalline precipitate was collected after cooling and then recrystallised from a mixture of alcohol and acetone, m. p. 178° (after drying in *vacuo* at 100°), yield 0·8 g. (Found: C, 50·57; H, 8·1; N, 15·66, 15·5, 15·7. $C_{11}H_{20}O_2N_3Cl$ requires C, 50·48; H, 7·7; N, 16·0 per cent).

Chaksine bromide was prepared similarly with barium bromide in theoretical yield. It was crystallised successively from water and a mixture of alcohol and acetone, m.p. 186° (after drying in *vacuo* at 100°). (Found: C, 43·3; H, 6·8; N, 13·34, 13·26. $C_{11}H_{20}O_2N_3Br$ requires C, 43·2; H, 6·5; N, 13·7 per cent). The C_{12} formula requires C, 47·6 per cent.

Chaksine Nitrate.—Chaksine iodide (2 g.), dissolved in water (20 c.c.), was decomposed with silver nitrate solution (1·2 g. in 10 c.c. of water) or potassium nitrate solution by warming on the steam-bath for 10 minutes. After filtration, the nitrate crystallised on cooling. It was recrystallised in transparent rectangular plates from hot water and then from alcohol. The substance after dehydration in *vacuo* lost its transparency and had m. p. 220° (decomp.). (Found: C, 45·8, 45·85; H, 6·91, 7·2; N, 19·3, 19·2, 19·5. $C_{11}H_{20}O_5N_4$ requires C, 45·8; H, 6·9; N, 19·44 per cent).

Nitrochaksine Sulphate.—To ice-cold sulphuric acid (2·5 c.c.) was added chaksine nitrate (0·9 g.) in small quantities at a time. The mixture was stirred for ½ minute and then poured to ice. The precipitate was crystallised from hot-dilute alcohol, m. p. 176° (decomp.). This substance partially decomposes on drying in *vacuo* at 140°. (Found after drying at 110°: C, 39·8; H, 6·5; N, 16·4, 16·5 per cent). The nature of this substance is being investigated.

Action of Nitrous Acid on Chaksine Chloride.—To an ice-cold solution of chaksine chloride (1 g.) in water (15 c.c.) was added a solution of sodium nitrite (0·5 g.) in water (5 c.c.) and the mixture acidified with hydrochloric acid. A substance separated out almost immediately. The mixture was heated to boiling to dissolve the precipitate and then was allowed to cool. The colourless substance now separating was collected and crystallised from water and then from alcohol. During the action no evolution of nitrogen was noticed. The substance (transparent plates) had m. p. 221° (decomp.). (Found: C, 45·7, 46·01; H, 7·04, 7·06; N, 18·8, 18·78 per cent).

Oxidation of Chaksine Sulphate with Hydrogen Peroxide.—To a solution of chaksine sulphate (3 g.) in water (250 c.c.) warmed to 80° were added a few drops of ferrous sulphate solution. When the temperature of the

mixture was 58°, hydrogen peroxide (15 c.c.) was added gradually avoiding further rise in temperature. The mixture was distilled and the distillate bubbled through an alcoholic solution of dimethyldihydroresorcin. After acidification of the dimedon solution with acetic acid, it was refluxed for 3 hours. The precipitate was treated with benzene and then precipitated with petrol ether. After rejecting the first precipitate, the solution on concentration gave needles which after crystallisation from hot petroleum ether had m. p. 188° and was identified as the formaldehyde condensation product. There is evidence of other substances being formed and these are under investigation.

Oxidation of Chaksine Sulphate with Potassium Permanganate in Alkaline Medium.—A solution of sodium hydroxide (2·5 g.) in water (15 c.c.) was added gradually under cooling to a solution of chaksine sulphate (7 g.) in water (300 c.c.). To this solution was then added gradually and with thorough shaking, during 1 hour, potassium permangnate solution (200 c c., 5%) and the temperature during addition was maintained at 30°. The mixture was allowed to stand at room temperature for 2 hours and then filtered, the precipitate being washed several times with hot water. The filtrate and the washings were mixed together and concentrated in *vacuo*, and the distillate was trapped in hydrochloric acid, whence ammonium chloride was isolated and identified.

The concentrated mother-liquor was strongly acidified with concentrated sulphuric acid and then extracted repeatedly with ether. The ethereal extract after dehydiation over anhydrous sodium sulphate and removal of the solvent, gave a liquid which was acidic in reaction. The acidic liquid was esterified and fractionated. From the first fraction oxalic acid was isolated after hydrolysis and identified (mixed m. p. 98-99°). The second fraction, b.p. 80°/3 mm., analysed as follows: (Found: C, 60·02; H, 9·49. $C_{10}H_{18}O_4$ requires C. 59·4; H, 8·9 per cent). The third ester, b.p. 100-105°/3 mm., gave C, 57·35; H, 8·9. $C_4H_9OCOOC_2H_5$ requires C, 57·5; H, 9·5 per cent.

SYNTHESIS OF BENZONICOTINE.

By B. K. NANDI.

A synthesis of benzonicotine has been described starting from ethyl quinoline-3-carboxylate and N-methylpyrrolid-2-one according to Späth's synthesis of nicotine from ethyl pyridine-3-carboxylate.

Späth's synthesis of nicotine from ethyl pyridine-3-carboxylate suggested the possibility of synthesising a compound from ethyl quinoline-3-carboxylate (Friedländer and Gohring, *Ber.*, 1884, **17**, 459; Stuart, *J. Chem. Soc.*, 1888, **53**, 143; Tafel and Wassmuth, *Ber.*, 1907, **40**, 2831) which could similarly be reacted with N-methylpyrrolid-2-one to give a benzonicotine (VII).

N-methylpyrrolid-2-one (II) (Tafel and Wassmuth, *loc. cit.*, Späth and Bertschneider, *Ber.*, 1928, **61**, 327) has been condensed with ethyl quinoline-3-carboxylate (I) in presence of alcohol-free sodium ethylate to 3′ : N′-methylpyrrid-2-onyl-3-quinolyl ketone (III). This is then converted into 3-quinolyl-γ-methylamino-n-propyl ketone (IV) by hydrolysis with

(I)   (II)   (III)

(IV)   (V)

(VI)   (VII)

* In the above formulæ R stands for

fuming hydrochloric acid. The amino-ketone is subsequently reduced catalytically to 3-quinolylamino-*n*-propyl carbinol (V) in poor yield. On treatment with red phosphorus and hydriodic acid, the iodo derivative, α-3-quinolyl-ε-methylamino-*n*-butyl iodide (VI), is obtained which passes into the racemic benzonicotine (VIII) in potassium hydroxide solution.

Benzonicotine containing an asymmetric carbon atom (C*) like nicotine, should have two optical isomers. In the racemic form the new base has been physiologically tested and has been found to be one-third as active as natural *l*-nicotine. The detailed experiments of its pharmacology are being published elsewhere.

<center>E X P E R I M E N T A L.</center>

3′ : *N′-Methylpyrrid-2-onyl-3-quinolyl Ketone.*—To alcohol-free sodium ethylate (6 g.) in benzene (20 c.c.) was added ethyl quinoline-3-carboxylate (10 g.) dissolved in *N*-methylpyrrolid-2-one (4·9 g.). The mixture was kept at ordinary temperature for 24 hours (exclusion of moisture) during which time it assumed a dark brown colour. After the addition of more benzene (5 c.c.) it was refluxed on the water-bath for 9 hours when a solid brown mass was obtained. To this sufficient ice-cold water was added to dissolve the whole mass The clear solution was then shaken with ether to remove any unreacted substance and the aqueous layer acidified to congo-red paper with dilute acetic acid, when a yellowish dense turbidity was obtained. The product was extracted with chloroform, the chloroform extract dried over calcium chloride and the solvent distilled off. A brown oil was left behind which solidified on leaving overnight in vacuum desiccator, yield 6 g. It crystallised in plates from dry benzene. m. p. 120°. It is soluble in ether and alcohol and sparingly in ligroin. (Found : C, 70·44; H, 5·60; N, 11·16. $C_{15}H_{14}O_2N_2$ requires C, 70·86; H, 5·51; N, 11·02 per cent).

The *monopicrate* was prepared by dissolving the substance in alcohol and adding an alcoholic solution of picric acid (1 mol.), when the picrate separated readily. It crystallised in shining yellow needles from alcohol, m. p. 178°. (Found : N 14·52. $C_{15}H_{14}O_2N_2, C_6H_3O_7N_3$ requires N, 14·49 per cent).

3-*Quinolyl-γ-methylamino*-n-*propyl Ketone.*—The β-diketone (4 g.) was heated in a sealed tube with fuming hydrochloric acid (40 c. c.) at 140-145° for 7 hours. The solution was then diluted with water and made alkaline with sodium carbonate when a turbidity was obtained. After extraction with ether in the continuous extraction apparatus, the ether

extract was dried over sodium sulphate and the ether removed. A brown oil was obtained which distilled at 165-75°/0·01 mm. The ketone is sparingly soluble in water, more so in alcohol and ether and freely in chloroform. (Found : C, 73·55 ; H, 6·93 ; N, 12·30. $C_{14}H_{15}ON_2$ requires C, 73·69; H, 7·01 ; N, 12·28 per cent).

The *chloroplatinate* of the ketone was obtained by dissolving the substance in 10% hydrochloric acid and adding a solution of platinic chloride when the salt separated on concentration and cooling. It crystallised from dilute alcohol (75%) in pale brown needles, m. p. 215-20°. (Found : Pt, 30·38. $C_{14}H_{15}ON_2$, H_2PtCl_6 requires Pt, 30·56 per cent).

3-Quinolyl-γ-methylamino-n-*propyl Carbinol*—The reduction of the 3-quinolyl-γ-methylamino-n-propyl ketone (5 g.) dissolved in hydrochloric acid (10%, 30 c c.) to the alcohol was effected by hydrogen in presence of palladised charcoal from 25 c.c. of 1% palladium chloride solution and 4 g. of "extra norite." About 700 c.c. of hydrogen were absorbed (theoretical 740 c.c.) in 8 hours, after which there was no further absorption. The filtrate from the mixture was made alkaline to litmus with sodium carbonate solution, when an oily substance separated which was extracted with ether by the continuous process and a reddish oil obtained after removal of ether, yield 3·5 g. The oil is fairly soluble in water and very soluble in alcohol, ether, acetone and benzene, b.p. 200-4°/0·5 mm.

The *chloroplatinate* of the base was formed by dissolving the substance in 10% hydrochloric acid and adding platinic chloride solution in excess. The platinum salt crystallised from alcohol in needles, m.p. 286-88°. (Found: Pt., 30·31. $C_{14}H_{18}ON_2$, H_2PtCl_6 requires Pt, 30·46 per cent).

The *dipicrate*, prepared in the usual way, crystallised from alcohol, m.p. 199-201°. (Found: N, 16·17. $C_{14}H_{18}ON_2$, $2C_6H_3O_7N_3$ requires N, 16·27 per cent).

α-3-Quinolyl-δ-methylamino-n-*butyl Iodide* and *r-Benzonicotine.*—3-Quinolyl-γ-methylamino-n-propyl carbinol (3 g.) and hydriodic acid (d 1·94, 45 c.c.) and red phosphorus (5 g.) were heated under reflux in an oil-bath at 100-110° for 4 hours. The excess of hydriodic acid was then removed in vacuum at 50°. To the residue were added 35 c.c. of water and the solution filtered off from the red phosphorus, neutralised with potassium carbonate solution and then 40 c.c. of 10% potassium hydroxide added.

α-3-Quinolyl-δ-methylamino-n-butyl iodide was converted on standing for 24 hours into r-benzonicotine, when the clear solution became

densely turbid and was reddish brown in colour. The whole was then extracted with ether continuously, the ether extract dried over sodium sulphate and the ether distilled off. The light brown oily residue (1·8 g.) distilled at 172-175°/0·1 mm. as a colourless oil which assumes a brown colour when left exposed to air. (Found: C, 78·98 ; H, 7·43 ; N, 13·17. $C_{14}H_{16}N_2$ requires C, 79·24 ; H, 7·54 ; N, 13·20 per cent). Unlike nicotine, benzonicotine is not volatile in steam, and is slightly soluble in water.

The *dipicrate* was obtained in ether with an alcoholic solution of picric acid in excess when the salt separated. It crystallised in yellow silky needles from ethyl alcohol, m.p. 224-25°. The picrate is sparingly soluble in both methyl and ethyl alcohol, acetone and chloroform, and insoluble in benzene. (Found: N, 16·78. $C_{14}H_{16}N_2$, $2C_6H_3O_7N_3$ requires N, 16·71 per cent).

The *chloroplatinate*, prepared in 10% hydrochloric acid solution of the base with excess of platinic chloride solution, is very sparingly soluble in alcohol, acetone, chloroform, and insoluble in benzene. It crystallised in light yellow crystals from ethyl alcohol, m.p. 232-34°. (Found: N, 4·59; Pt, 30·98 $C_{14}H_{16}N_2$, H_2PtCl_6 requires N, 4·50; Pt, 31·35 per cent).

The *chloro-aurate* crystallised in shining yellow needles from alcohol, m.p. 239-40° (decomp.).

THE ALKALOID OF *BERBERIS UMBELLATA*, WALL. PART I. ISOLATION AND EXAMINATION OF UMBELLATINE.

By R. Chatterjee.

From the stem bark of *Berberis umbellata* a new alkaloid of the molecular formula $C_{21}H_{21}O_8N$ has been isolated. It contains one methylenedioxy group, two methoxy groups and one imino group. The new alkaloid has been designated as umbellatine.

Berberine and several other alkaloids have been reported to be present in various species of the genus *Berberis* (N.O. Berberidaceae). An examination of *B. umbellata* has now been carried out with a view to find whether it contains any new alkaloid or not. The stem bark was collected from Darjeeling District in July. It has yielded a yellow crystalline alkaloid, m.p. 206-7° (decomp.). The analytical data are in agreement with the molecular formula $C_{21}H_{21}O_8N$. As it appears to be a new alkaloid, it has been named "umbellatine."

Umbellatine has been found to contain two methoxy groups. It forms a crystalline methiodide and a yellow nitroso derivative which points to the presence of the nitrogen atom as a secondary amine ; 5% gallic acid solution imparts a green colour to a solution of umbellatine in concentrated sulphuric acid, indicating the presence of a methylenedioxy group. The analytical data show the presence of one methylenedioxy group. It crystallises from water with 5·5 molecules of water of crystallisation, it contains half a molecule of water even on drying in *vacuo* at 110° and on raising the temperature to 120°, the colour of umbellatine changes from yellow to light brown. At higher temperatures umbellatine decomposes gradually ; hence its remaining half molecule of water cannot be removed

Experimental.

Isolation of Umbellatine.—The finely ground air-dried stem bark (1 kg.), obtained from Messrs. G. Ghose & Co., Darjeeling, was extracted by cold percolation with 90% alcohol during 10 days. The dark brown residue, after the removal of alcohol on the water-bath, was treated with cold water (500 c.c.) and filtered. The filtrate was extracted with light petroleum (b.p. 40-60°), to remove some oily matter. Moderately concentrated hydrochloric acid was then added to the aqueous extract to give 1% solution, which was allowed to stand for 2 hours. The crude hydrochloride of the

alkaloid gradually crystallised out and.was filtered off.   It was recrystallised from hot water as yellow, feathery needles, decomposing above 200°, yield 8·5 g.

The *hydrochloride* (5 g.) was dissolved in hot water and made alkaline with sodium hydroxide solution, when a yellow precipitate was obtained. It was collected and crystallised from hot water in yellow silky needles, m.p. 206-7° (decomp.). The yield of pure umbellatine is 0·68% calculated on the amount of air-dried bark. [Found in a sample dried at 110° in *vacuo* over P_2O_5: C, 59·0, 58·8 ; H, 5·33, 5·36 ; N, 3·2, 3·3 ; OMe, 14·4 ; CH_2O_2, 2·95 (Clowes and Tollens, *Ber.*, 1899, **32**, 2841). Found in a sample dried at 120° in *vacuo* over P_2O_5 : C, 58·8 ; H, 5·33. $C_{21}H_{21}O_8N$, $\frac{1}{2}H_2O$ requires C, 59·4 ; H, 5·2 ; N, 3·3 ; OMe, 14·62 ; CH_2O_2, 3·30 per cent].

Umbellatine is optically inactive. It is soluble in alcohol, methanol and hot water, sparingly soluble in cold water, acetone and chloroform and insoluble in benzene, ethyl acetate, ether and light petroleum ether.

Umbellatine forms crystalline hydrochloride, hybrobromide and hydriodide. Reactions with alkaloidal reagents are tabulated below :

Mayer's reagent	Pale yellow precipitate formed immediately.
Wagner's reagent	Orange precipitate formed immediately.
Picric acid	Pale yellow precipitate.
10% Potassium iodide solution ...	Yellow precipitate.
Acidified with conc. H_2SO_4 in a test tube and brought in contact with Cl_2 water	A blood red ring at the junction of the layers of two liquids
Concentrated sulphuric acid ...	Dissolves with deep yellow colour changing to green.
Erdmann's reagent	Dissolves with a violet colour changing to blood-red and finally to yellow on long standing.
Frohde's reagent	Dissolves with a greenish yellow colour.
Mandelin's reagent	Yellow colour changing to red.
Conc. H_2SO_4 with $K_2Cr_2O_7$ powder	Green colouration on long standing.

Umbellatine Hydrochloride.—To a solution of umbellatine in hot water dilute hydrochloric acid was added drop by drop, till the precipitated hydrochloride settled down. On rewarming the mixture the hydrochloride dissolved and on cooling it crystallised as yellow feathery crystals, which charred without melting.

Umbellatine Chloroplatinate.—The chloroplatinate, prepared with a warm concentrated solution of umbellatine hydrochloride (0.3 g.) in water and platinic chloride (0·12 g.), separated as a yellow granular precipitate which was collected after heating on the water-bath for about 15 minutes. The

precipitate was well washed with hot water, and then collected and dried. Umbellatine chloroplatinate is a light yellow powder, which is insoluble in organic solvents and water, and which decomposes without melting. [Found: Pt, 15·71; M. W. 415. $(C_{21}H_{21}O_8N, HCl)_2 PtCl_4$ requires Pt, 15·72 per cent. M. W. 415].

Nitrosoumbellatine.—An ice-cold solution of umbellatine (1 mol) in 10% acetic acid solution was treated with an ice-cold solution of sodium nitrite (1.5 mol.). A yellow granular precipitate was obtained, which was filtered after keeping the reaction mixture overnight at room temperature and was well washed first with 5% acetic acid solution and then with water. The nitroso derivative crystallised from alcohol in yellow glistening needles, m.p. 265-67° (decomp.). (Found: N, 6·9. $C_{21}H_{20}O_9N_2$ requires N, 6·4 per cent).

Umbellatine Methiodide.—A solution of umbellatine (1 mol.) in chloroform and methyl iodide (1·5 mol.) was allowed to stand at the room temperature for about 2 hours when a yellow crystalline methiodide separated. It was filtered, well washed with chloroform and dried; it chars without melting.

Further work is in progress.

The author is indebted to Mr. N. Ghosh, for some of the analyses recorded in this paper. The author extends his thanks to Miss A. Mukherjee and Dr. P. K. Bose for their kind interest in the work and to Dr. D. Chakravarti of the University College of Science and the very Rev. Father A. Schockaert, S. J., Rector, St. Joseph's College, Darjeeling, for affording him laboratory facilities.

THE INFLUENCE OF SUBSTITUTION ON THE FORMATION OF DERIVATIVES OF a-HYDRINDONE AND a-TETRALONE. SYNTHESIS OF 1:2:3:4-TETRAHYDRO-NAPHTHALENE-1:2-DICARBOXYLIC ACID.

By Nripendra Nath Chatterjee and Girindra Nath Barpujari.

The present investigation describes a method for the synthesis of 1:2-dicarboxy-1:2:3:4-tetrahydronaphthalenes, which are important for the synthesis of benzanthracene derivatives with carcinogenic property.

Benzaldehyde cyanohydrin is allowed to react with the sodium salt of ethyl cyanoacetate and the sodium derivative of ethyl $a\beta$-dicyano-β-phenyl-propionate (I, R=R'=H) is allowed to react when with ethyl chloroacetate diethyl $a\beta$-dicyano-a-phenyl-n-propane-βr-dicarboxylate (I, R' = H; R = $CH_2 \cdot CO_2Et$) is obtained. On hydrolysis with sulphuric acid (70%) the latter yields a-phenyl-n-propane-$a\beta r$-tricarboxylic acid, m.p. 204° (II, R=H). The acid (II, R=H), described by Hecht (Monatsh, 1903, 24, 371) melts at 110-115°, then solidifies and finally melts again at 196-201° and it is identical with a-pheny-tricarballylic acid, m. p. 199°, obtained by Stobbé and Fischer (Annalen, 1901, 315, 231, 245). Uncertain melting point is often characteristic of tribasic acids and is doubtless due to the formation of a small amount of anhydride. The acid (II, R=H) in presence of sulphuric acid · undergoes ring-closure to yield the keto-acid (III, R=CO). It is, however, possible that the product, instead of being tetrahydro-naphthalene derivative might be the hydrindone derivative (IV). On Clemmensen reduction it yields a gummy acid from which 1:2:3:4-tetrahydronaphthalene-1:2-dicarboxylic acid (III, R= CH_2) crystallises out on keeping in a vacuum desiccator over sulphuric acid for a long time The gummy acid might be a mixture of cis- and trans-tetrahydronaphthalenes or a mixture of naphthalene and hydrindone derivative.

a-(p-Methoxyphenyl)-n-propane-$a\beta\gamma$-tricarboxylic acid (II, R=OMe) obtained by hydrolysing diethyl $a\beta$-dicyano-a-(p-methoxyphenyl)-n propane-$\beta\gamma$-dicarboxylate (I, R'=OMe ; R=CH_2CO_2Et) on the other hand, under similar treatment does not cyclise but is sulphonated.

It has been shown by Thorpe and others (J. Chem. Soc., 1924, 2185) that phenylsuccinic acid undergoes ring-closure to yield 1-ketohydrindene-3-carboxylic acid. An extension of the method for the synthesis of

methoxy derivative of hydrindones has been abandoned as it is found that the ring-closure of p-methoxyphenylsuccinic acid or its ester does not take place with phosphorus pentoxide or with sulphuric acid.

p-Methoxyphenylsuccinic acid (*cf.* Baker and Lapworth, *J. Chem. Soc.* 1925, **127**, 560; Chrzaszesewska, *Roczniki Chem.*, 1925, **5**, 1, 33 ; Carson and Stoughtoun, *J. Amer. Chem. Soc.*, 1928, **50**, 2825) has been prepared by hydrolysing ethyl $\alpha\beta$-dicyano-β-(p-methoxyphenyl)-propionate (I, $R' =$ OMe ; $R = H$) with 20% sulphuric acid.

CN
|
CH—CR(CN)CO$_2$Et
(attached to benzene ring bearing R')

(I)

CO$_2$H
|
CH—CH—CO$_2$H
|
CH$_2\cdot$CO$_2$H
(attached to benzene ring bearing R)

(II)

CO$_2$H
CO$_2$H
(naphthalene-type ring, R)

(III)

CH$\cdot$CO$_2$H
CH$\cdot$CH$_2\cdot$CO$_2$H
CO
(indanone-type ring)

(IV)

EXPERIMENTAL.

Diethyl $\alpha\beta$-Dicyano-α-phenyl-n-propane-$\beta\gamma$-dicarboxylate (I, $R' = H$ $R = CH_2\cdot CO_2Et$).—Mandelic nitrile (66 g.) was added in small quantities at a time to an alcoholic suspension of sodio-cyanoacetate, prepared from ethyl cyanoacetate (56 g.), alcohol (140 c.c.) and sodium (11.6 g.). The temperature was regulated by cooling in ice-water. When all the nitrile had been added, a clear brown solution was obtained, which was allowed to stand for 12 hours. The mixture was mixed with ethyl chloroacetate (65 g.) and after the initial reaction had abated, was boiled under reflux for about 15 hours. The filtered liquid was diluted with water, dried and the ether moved. The dicyano-ester distilled as a viscous liquid, b.p. 205-207°/4 mm., yield 60 g. (Found : C, 65.3 ; H, 5.7. $C_{17}H_{18}O_4N_2$ requires C, 65.0; H, 5.7 per cent).

α-Phenyl-n-propane-$\alpha\beta\gamma$-tricarboxylic Acid (II, R=H).—The foregoing ester (40 c.c.) was mixed with sulphuric acid (70%, 240 c.c.) and boiled under reflux for 14 hours, the condenser being removed from time to time to allow the alcohol formed to escape. The cooled solution was then diluted with water, extracted with ether, and the ethereal extract treated

with sodium carbonate. The carbonate solution was acidified and extracted with ether. The acid obtained after removal of ether was heated on a water-bath with a solution of sodium hydroxide (15%) for 3-4 hours. The solution was extracted after acidification. The residue from ether was kept in a desiccator, when it solidified. It crystallised from water, m. p. 204°. (Found : C, 56·8 ; H, 4·5. Calc. for $C_{12}H_{12}O_6$: C, 57·1 ; H, 4·7 per cent).

The triethyl ester of the above was obtained in an almost quantitative yield from the acid (7 g.) absolute alcohol (30 c.c.), concentrated sulphuric acid (2 c.c.), 3 litres of vapourised alcohol (3-4 hours). After dilution with a large volume of water, the ester was extracted with ether, the ethereal solution was shaken with sodium bicarbonate solution and washed again, dried with sodium sulphate and ether removed. It was distilled at 185-190°/5 mm., yield 6· g. (Found : C, 64·0 ; H, 7·1. $C_{18}H_{24}O_6$ requires C, 64·3 ; H, 7·1 per cent).

1-Keto-tetrahydronapthalene-3 : 4-dicarboxylic Acid (III, R = CO).—The acid (II, R = H ; 5 g.) was heated with sulphuric acid (d 1. 84, 20 g.) on the water-bath for 2 hours. The product was poured into ice and after working up in the usual manner was crystallised several times from water, m. p. 179-82°, yield 1.5 g.. (Found : C, 61.4; H, 4.3. $C_{12}H_{10}O_5$ requires C, 61.5; H, 4.2 per cent).

Oxidation of 1-Ketotetrahydronaphthalene-3: 4-dicarboxylic Acid.—The acid (4 g.) in sodium hydroxide solution, was heated on the steam-bath and oxidised with a warm saturated solution of potassium permanganate until the colour persisted. After destroying the excess of permanganate, the solution was filtered and the filtrate acidified and extracted with ether, the ethereal extract yielded phthalic acid, which after crystallisation from water was identified by mixed m.p.

1:2:3:4-Tetrahydronaphthalene-1:2-dicarboxylic Acid (III, R = CH₂).— The pure keto-acid (5 g.), amalgamated zinc (40 g.), and concentrated hydrochloric acid (40 c.c.) were refluxed for 12 hours, more acid (40 c.c.) was then added and the heating continued for 12 hours. The gummy product, obtained after working up in the usual manner, was kept in a vacuum desiccator over sulphuric acid for a long time, when a small quantity of an acid crystallised out, m.p. 193° (rapid heating). (*cf.* Auwers and Möller, *J. pr. Chem.*, 1925, *ii*, **109**, 124). (Found : C, 65·2; H, 5·4. Calc. for $C_{12}H_{12}O_4$: C, 65·4; H, 5·5 per cent).

Diethyl αβ-Dicyano-α- (p-methoxyphenyl)-n-propane-βγ-dicarboxylate (I, R′ = OMe ; R = CH₂CO₂Et).—Anisaldehyde cyanohydrin (68 g.) was

gradually added to the alcoholic suspension of sodiocyanoacetate, prepared from ethyl cyanoacetate (56 g.), alcohol (140 c.c.) and sodium (11·6 g.) Considerable heat was generated after each addition and the temperature was regulated by cooling. The clear brown solution was allowed to stand for 12 hours and the mixture mixed with ethyl chloroacetate (70 g.) and after the initial reaction had abated, was boiled under reflux for about 15 hours. It was filtered and washed with dry ether, the filtrate diluted with water and extracted with ether; the ethereal solution was washed with water, dried and the ether removed. The dicyano-ester distilled as a viscous liquid, b.p. 232-37°/3 mm., yield 40 g. (Found: C, 63·1; H, 5·9; $C_{18}H_{20}O_5N_2$ requires C, 62·8; H, 5·8 per cent).

α- (p-*Methoxyphenyl*)-n-*propane-αβγ-tricarboxylic Acid* (II, R=OMe) —A solution of the above cyano-ester (20 g.) in concentrated sulphuric acid (22 c.c.) was diluted with water (320 c.c.) and refluxed for 50 hours on a sand-bath. After cooling, the mixture was diluted with water and extracted with ether. The ether solution was dried with anhydrous sodium sulphate and the solvent removed. It was crystallised from water, m.p. 190° (rapid heating), yield 8 g. (Found: C, 55·13; H, 4·8 Equiv., 95·0. $C_{13}H_{14}O_7$ requires C, 55·3; H, 4·9 per cent Equiv., 94·0).

The triethyl ester of the above acid was obtained in an almost quantitative yield by the alcohol vapour method from the acid (20 g.) absolute alcohol (100 c.c.), concentrated sulphuric acid (7 c.c.), 3 litres of vapourised alcohol (3-4 hours). After dilution with a large volume of water the ester was extracted with ether; the ether solution was shaken with sodium bicarbonate solution and washed again, dried with sodium sulphate and ether removed. It distilled at 210-15°/5 mm., yield 18 g. (Found C, 62·6; H, 6·9. $C_{19}H_{26}O_7$ requires C, 62·29, H, 7·1 per cent).

Ethyl αβ-Dicyano-β-(p-methoxyphenyl)-propionate (I, R′=OMe; R=H) It was obtained by the condensation of anisaldehyde cyanohydrin (55 g. with sodioethyl cyanoacetate as before. The clear solution obtained on keeping overnight was poured into water and the solution acidified with hydrochloric acid and the oil extracted with ether, the ethereal solution was washed several times with water to remove most of the alcohol, then thoroughly with a dilute solution of sodium carbonate and after drying over calcium chloride ether was evaporated. The dicyano ester distilled as a viscous liquid, b.p. 225°/5 mm., solidifying in a vacuum desiccator over sulphuric acid. It crystallised from alcohol as colourless crystals m.p. 81°, yield 30 g. (Found: N, 11·1. $C_{14}H_{14}O_3N_2$ requires N, 10·85 per cent).

p-*Methoxyphenylsuccinic Acid*.—A solution of the above cyano-ester (40 g.) in concentrated sulphuric acid (45 c.c.) was diluted with water (320 c.c.) and refluxed for 40 hours on a sand-bath. After cooling, the crystals separated which were filtered and crystallised from hot water, m.p. 205°. (Found: C, 59·3; H, 5·2. Calc. for $C_{11}H_{12}O_5$: C, 58·9 ; H, 5·4 per cent). . -

p-*Methoxyphenylsuccinic Anhydride*.—The above acid was boiled with acetyl chloride for 1 hour and after removing acetyl chloride in a vacuum desiccator over caustic potash, it was obtained as crystals, m.p. 91° (mixed m.p.).

Diethyl (p-*methoxyphenyl*)*succinate* was obtained by refluxing the acid (15 g.) with alcohol (100 c.c.) in presence of concentrated sulphuric acid (15 g.) for 5 hours, b.p. 185°/4 mm., yield 15 g. (Found: C, 64·6; H, 6·9. $C_{25}H_{20}O_5$ requires C, 64·3 ; H, 7·1 per cent).

COMPOUND FORMATION IN SOLUTIONS. PART I.
PYRIDINE AND ACETIC ACID.

By S. Venkataraman.

Singularities in physical properties accompanying compound formation in binary liquid mixtures are discussed, and it is pointed out that a maximum in viscosity-concentration curve is not a conclusive evidence of compound formation. Intensity and depolarisation of scattered light and magnetic susceptibilities of pyridine-acetic acd mixtures of different concentrations are determined and these experiments seem to indicate the formation of a chemical complex containing 60 mol. % of the acid and 40 mol. % of pyridine. Viscosity-concentration curve, however, shows a maximum for a mixture containing 78 mol % of the acid.

Two liquids having considerable affinity for each other combine to form a chemical complex when mixed. All cases of compound formation in solutions are accompanied by certain singularities in physical properties of the mixture, those that were mostly studied being, heat of solutions, density, viscosity, surface tension, vapour pressure and refractive index. Particularly viscosities of solutions were widely studied to consider compound formation (Hatschek, " Viscosity of Liquids", 1928 Chapter IX).

The early work on the viscosity of binary mixtures was to find out the law of " ideal " mixtures which has, however, proved elusive so far. The large amount of experimental data accumulated show that most mixtures exhibit viscosity maxima for a particular concentration of the components. Dunstan and his collaborators (Dunstan and Thole, " Viscosity of Liquids' , 1917, p. 44) have pointed out that components of mixtures showing maxima in their viscosity-concentration curves are generally those which have a considerable affinity for each other and therefrom conclude that a maximum in viscosity-concentration curve should be regarded as indicating compound formation between the components in the mixture. The prodigious amount of experimental results supplied by Dunstan and co-worker (*J. Chem. Soc.*, 1904, **85**, 817; 1907, **91**, 1728 ; 1913, **103**, 1108) Tsakalatos (*Bull. Soc. chim.*, 1908, iv, **3**, 134) and others seem to point out that the above view is fairly conclusive. This view is supported by actual demonstration of compound formation ; we know from chemical evidence, that a hydrate is formed when acetic acid and water are mixed in the ratio of about 80% by weight of the acid to about 20% by weight of water. Viscosity-concentration curve also shows a maximum in mixture containing 80% by weight of the acid,

In liquid mixtures, besides the large change in viscosity that indicates formation of chemical complexes, there are other singularities in physical properties, which also seem to indicate the same chemical combination. In acetone-chloroform mixture a minimum in the vapour pressure curve (Zawidzki, Z. physikal. Chem., 1909, **39**, 129) occurs for about the same proportion of the components giving a viscosity maximum (Faust, ibid., 1912, **79**, 97) ; a maximum deviation from the mixture law values of magnetic susceptibilities (Buchner, Nature, 1931, **128**, 301 ; Ranganadham, Indian J. Phys., 1931, **6**, 421) is also exhibited for the same proportion of the components. Density determination of acetic acid-water mixture (Oudemans, L. B. M. Tables) indicates a maximum density at 80% by weight of the acid. Krishnamurti's work (Indian J. Phys., 1931, **6**, 401) on Raman-effect in acetic acid solutions shows the appearance of a new line (1707 cm.$^{-1}$) and the disappearance of the line (1667 cm.$^{-1}$) originally present, when the concentration reaches 77% of the acid. The magnetic susceptibilities of acetic acid-water mixtures determined by Sibaiya and Venkataramaiah (Indian J. Phys., 1932, **7**, 393) also show a maximum deviation from the mixture law relations for the same proportion of the components.

'A comparison of the viscosity and vapour pressure data available shows that for a maximum in the viscosity curve of a certain mixture, there corresponds a minimum in the vapour pressure curve and vice versa (cf. Faust, loc. cit.; Yajnik, Bhalla, Talwar and Soofi, Z. physikal. Chem., 1925, **118**, 305). Mixtures of pyridine and aniline with acetic acid show maxima in viscosity curves and minima in vapour pressure curves ; and the mixture of acetone and carbon disulphide shows a viscosity minimum and vapour pressure maximum. Zawidzki (loc. cit.) has shown that pyridine-water mixture behaves anomalously, as both viscosity and vapour pressure curves show maxima. This is explained by supposing that the compound formed in solution is dissociated to the extent of 96% in the vapour. Krishna-murti's work (loc. cit.) shows that a compound is formed when the liquids are mixed in the proportion necessary to produce viscosity maximum.

The vapour pressure data by Zawidzki for acetic acid-pyridine mixtures show an anomalous behaviour, as the vapour pressure curve indicates a minimum for a mixture containing 50 mol. % of the acid and two points of inflexion corresponding to mixtures containing 30 and 80 mol. % of the acid. He suggests the possibility of the existence of two compounds, one containing more pyridine corresponding to the first point of inflexion and the other containing more acid corresponding to the second point of inflexion. Viscosity curve shows only one maximum at 78 mol. % of the acid, while

the density of the mixture is a maximum at 86 mol. % of the acid. But according to Hatschek ("Viscosity of Liquids," 1928, p. 248) there is considerable evidence to show the formation of a compound containing three molecules of acetic acid and two of pyridine, *i.e.*, in a mixture containing 60 mol. % of the acid. Hence this work was undertaken to see if other physical properties of the mixture show any singularities indicating compound formation.

Among the physical properties which have not been widely used so far, are the intensity and depolarisation of light scattered by solutions. Ostwald (*Trans. Faraday Soc.*, 1913, **9**, 43) showed a parallelism between the viscosity and opalescence of partially miscible liquids as critical solution temperature is approached. Rav (*Proc. Indian Assoc. Cult. Sci.*, 1924, **9**, 13) has shown that the intensity of light scattered exhibits a maximum for a particular concentration, while the depolarising factor shows a minimum for another concentration. To verify his formula for scattering in binary mixtures, selection of liquids was arbitrary and the mixtures were not those that were likely to form chemical complexes. Hence the study of the variation of depolarising factor and the intensity of the scattered light in acetic acid-pyridine mixtures, in which a compound is supposed to exist, has been undertaken.

EXPERIMENTAL.
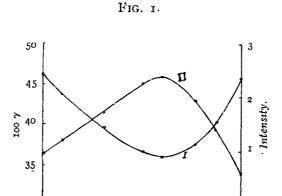
Light Scattering in Acetic Acid-pyridine Mixtures.

Measurement of Depolarisation.—The liquids employed were rendered dust-free by the method originally used by Martin and others (*J. Phys. Chem.*, 1920, **24**, 478 ; *cf.* also Raman and Seshagiri Rao, *Phil. Mag.*, 1923, **45**, 625). Several bulbs containing dust-free pure liquids and solutions of known concentrations, including those with 60, 78 and 86 mol. % of the acid were prepared. (A large amount of heat is given off on mixing the pure liquids presumably indicating compound formation).

Sunlight was reflected by means of a heliostat on the object glass of a telescope (aperture 4″, focal length, 1 meter), placed in a dark room. The bulbs were immersed one after another into a rectangular tank (the outside of which was blackened leaving only three windows as in the case of the bulbs) containing distilled water The narrow intense beam of sunlight emerging out of the tube of the telescope was made to pass axially through the bulb immersed in the tank.

The depolarising factor, γ, of the scattered light was measured by means of a double image prism and nicol in the usual manner (Wood, " Physical

Optics," 3rd Ed., p. 432). The results obtained (curve I, Fig. 1), indicate a minimum in the depolarisation-concentration curve, which occurs in a mixture containing 60 mol. % of the acid.

FIG. 1.

Mol. % acid

Intensity Measurements.—The same bulbs were used for the measurement of the intensity of scattered light. The bulb containing pyridine was used as the standard. The other bulbs were placed one after another, in contact with and by the side of the pyridine bulb, so that the light passed straight through the bulbs. A rotating sector photometer (Hilger's) was used for the measurement of intensity. The intensity-concentration curve (curve II, Figure 1), shows a maximum for the mixture showing a minimum in the γ-concentration curve.

Measurement of Magnetic Susceptibility.—Quincke's method was used for the determination of the magnetic susceptibilities of the mixtures. Two uniform capillary tubes, of not too narrow a bore, were supported vertically between the flat pole pieces of a large Pye's electromagnet specified to carry a maximum current of 12 amps. Each capillary tube was connected at both ends to a wider tube, about a foot away, by glass tubing so as to form a closed system. One of the capillary tubes contained pure distilled water, whose susceptibility was assumed to be -0.720×10^{-6}. The other tube was for liquids to be experimented upon.

If δ is the depression of the meniscus in any one of the tubes on switching on the current, then the specific susceptibility χ of the liquid in it is given by the relation,

$$\chi = \frac{2\delta g}{H^2} + \frac{\rho_0}{\rho}\chi_0$$

where H is the magnetic field, ρ, the density of the liquid, ρ_0 and χ_0, are the density and susceptibility respectively of the air-vapour mixture above the meniscus. The above relation reduces to

$$\chi = \frac{2\delta g}{H^2}$$

as the second term on the right is negligibly small compared to the first. If χ_1, δ_1 are the susceptibility and depression in the meniscus in the case of water in one of the tubes, and χ_2 and δ_2 stand for the same quantities in the case of the liquid in the other tube, we have

$$\frac{\chi_1}{\chi_2} = \frac{\delta_1}{\delta_2}$$

whence χ_2 can be calculated assuming χ_1.

To make sure that the results obtained by this method are reliable certain liquids, *viz.*, benzene, chloroform, carbon tetrachloride, acetic acid, and pyridine, whose susceptibilities are definitely known, were first used for investigation and the results obtained agree quite closely with the standard values in the International Critical Tables.

The bulbs used in the previous experiments were opened and the susceptibilities of the mixtures contained in them were determined. In Table II the experimental results are recorded in the third column and the second column gives the values for the corresponding mixtures calculated from the additive law. The last column gives the percentage deviation from the mixture law values. The maximum deviation occurs in a mixture containing 60 mol.% of the acid.

TABLE I.

Mixture (Mol % acid).	Susceptibility Calc.	Found.	% Deviation.
0	...	$-0\cdot637 \times 10^{-6}$	...
10	$-0\cdot627 \times 10^{-6}$	$-0\cdot625$	$0\cdot319$
30	$-0\cdot603$	$-0\cdot611$	$1\cdot33$
50	$-0\cdot578$	$-0\cdot590$	$2\cdot08$
60	$-0\cdot569$	$-0\cdot588$	$3\cdot34$
78	$-0\cdot553$	$-0\cdot562$	$1\cdot63$
86	$-0\cdot527$	$-0\cdot535$	$1\cdot52$
100	...	$-0\cdot503$	...

DISCUSSION.

The depolarisation and intensity measurements of scattered light and magnetic susceptibility measurements indicate the existence of a chemical complex containing three molecules of the acid and two of pyridine. But the data for viscosity, density and vapour pressure do not confirm this conclusion. The viscosity maximum is obtained with a mixture containing 78 mol.% of the acid and density maximum with a mixture containing 86 mol.% of the acid. The suggestion put forward by Zawidzki and referred to earlier in this paper could not be verified, as physical properties other than vapour pressure, do not seem to show any singularities at points corresponding to the two points of inflexion in his vapour pressure curve.

It is interesting to note that viscosity maximum in this case does not definitely indicate compound formation. It is therefore to be doubted whether any maximum in a viscosity-concentration curve may be safely assumed to be due to the formation of a compound, although the converse that maximum occurs whenever there is chemical combination is generally held to be true. An objection similar to this was raised by Senter ("Outlines of Physical Chemistry", 1925, p. 342), in connection with alcohol-water mixtures. Kurnakow and his collaborators (Z. physikal. Chem., 1913, 23, 481), who do not consider the maxima which shift with temperature being sufficient evidence of compound formation, find a new type of graph characteristic of binary mixtures containing compounds. The graph consists of two branches convex to the concentration axis which meet at an angle at the maximum point. The composition corresponding to the maximum point is independent of temperature. Dunstan and Thole (loc. cit.) explain the shift of maxima with temperature thus: "The maximum will coincide with the composition of the compound formed only if the viscosity of the compound is greater than one or both the components and if all or a large portion of the components combine". Perhaps the lability of the compound formed might also account for the shift of maximum with temperature.

Hence, in the case of acetic acid-pyridine mixtures, it is possible that the greatest amount of the compound is formed in the mixture containing 60 mol.% of the acid, but the viscosity of the compound being less than one or both the components, it is not a maximum for this particular concentration. The further the addition of acetic acid, the more viscous the component, has the effect of increasing the viscosity till a maximum is reached at 78 mol.% of the acid.

The magnetic susceptibility data show deviations from mixture law values, being about 3·34% for a mixture containing 60 mol.% of the acid. This deviation is quite in accordance with theoretical expectation as the molecules of both pyridine and acetic acid are polar, associated and asymmetric.

The investigation will be extended to the study of Raman-effect and other physical properties of the mixture.

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THE REACTION BETWEEN AQUEOUS IODINE AND SODIUM FORMATE.

By W. V. BHAGWAT.

The reaction between aqueous iodine and sodium formate has been studied in the dark and the effect of various salts, such as KCl, NaCl, NH_4Cl, K_2SO_4, $NaNO_3$ and NH_4I investigated. It is observed that effect of the three chlorides is similar : velocity constant at first increases with the concentration of chlorides and then falls. It seems that though Cl'ions act as positive catalyst, K , Na' and NH_4' ions retard the reaction, the order being NH_4' > Na' > K'. It also appears that NaCl, KCl and NH_4Cl molecules likewise retard the reaction. The effect of iodide ion in NH_4I is comparable to that in KI. Temperature coefficient of the reaction in aqueous iodine is less than in presence of KI. The relation between intensity and velocity for this reaction in presence and absence of KI and other salts has been investigated and in all cases the relationship was found to be less than direct.

The dark reaction between sodium formate and iodine dissolved in potassium iodide was studied by Dhar (*J. Chem. Soc.*, 1917, **111**, 707) and by Doosag and Bhagwat (*J. Indian Chem. Soc.*, 1934, **11**, 331 ; *Z. anorg. Chem.*, 1934, **216**, 241). No work seems to have been done using aqueous iodine free from potassium iodide. In this paper the reaction between aqueous iodine and sodium formate has been investigated and the effect of various salts on this reaction is recorded.

TABLE I.

Dark reaction in absence of potassium iodide.

Conc. of I_2 = 0·001207N. Conc. of HCOONa = 0·48 g. per litre. 50 C.c. of each solution were mixed together and various quantities of the solid salt dissolved in it.

Temp.	Salt.	Amount.	K_1.	Temp.	Salt.	Amount.	K_1.
30·5°	KCl	0	0·00582	30·5°	$NaNO_3$	0	0·0058
		0·5	0·00630			0·9471	0·0050
		1·0	0·00650			1·6576	0·0046
		2·0	0·00493			2·16	0·0048
	NaCl	0	0·00580		KNO_3	0	0·0058
		0·5	0·00637			0·5	0·0052
		1·0	0·00514			1·1275	0·0051
						2·0	0·0049
	NH_4Cl	0	0 0058				
		0 3246	0·0064				
		0·9965	0·0046	24.	Conc. of I_2 = 0·00113N. Conc. of HCOONa		
		2·3631	0·0028		= 0·96 g. per litre.		
	K_2SO_4	0	0·0058				
		1·2320	0·0060		NH_4I	0	0·00400
		2·0144	0·0056			0·8280	0·000234

The results clearly show that the effect of the three chlorides is similar. The velocity coefficient in all cases passes through a maximum, showing that though Cl′ ion acts as positive catalyst, the cations actually retard the reaction, the order being $NH_4^{\cdot} > Na^{\cdot} > K^{\cdot}$. Moreover, the decrease in the velocity coefficient with the increased concentration of the chlorides shows that these molecules also retard the reaction, since the concentration of these molecules increases with the increased concentration of the salt with consequent decrease in the degree of dissociation.

K_2SO_4, KNO_3, and $NaNO_3$ retard the reaction, $NaNO_3$ showing the maximum effect, thus confirming the view that $Na^{\cdot}$ ion has a greater retarding effect than $K^{\cdot}$ ions on this reaction.

NH_4I like KI retards the reaction and when their results are expressed in terms of the concentration of iodide ion, retardation becomes proportional to it.

The first addition of KI causes remarkable fall in the velocity coefficient, but subsequent fall is proportional to the concentration of $K^{\cdot}$, as is evident from Table II.

TABLE II.

Conc. of HCOONa $= 5 \cdot 2612$ g. per litre. $I_2 = 0 \cdot 00123 N$. Temp. $= 30^c$.

Amount of KI.	K_1.	Ratio of K_1.		Ratio of $\frac{1}{K_1}$.	
0	0·00465	$\frac{1 \cdot 039}{0 \cdot 335}$	$= 3$	$\frac{0 \cdot 00351}{0 \cdot 00123}$	$= 2 \cdot 9$
0·335	0·00351	$\frac{2 \cdot 15}{1 \cdot 039}$	$= 2 \cdot 1$	$\frac{0 \cdot 00123}{0 \cdot 000562}$	$= 2 \cdot 1$
1·039	0 00123				
2·15	0·000562	$\frac{2 \cdot 15}{0 \cdot 335}$	$= 6 \cdot 3$	$\frac{0 \cdot 00351}{0 \cdot 000562}$	$= 6 \cdot 1$

The temperature coefficient of this reaction in presence of KI is recorded in a previous paper (*loc. cit.*) and K_{26}/K_{21} has the value of $2 \cdot 1$. In absence of KI the temperature coefficient falls and

$$K_{34}/K_{29} = \frac{0 \cdot 0140}{0 \cdot 0091} = 1 \cdot 53, \text{ whence } K_{26}/K_{21} = 1 \cdot 54$$

Decrease in the temperature coefficient in absence of KI is in accordance with our explanation that the acceleration of a reaction depends upon its initial velocity. Under same conditions, the velocity of reaction is greater in absence of KI than in its presence and hence the acceleration in absence of KI is smaller. The temperature coefficient is therefore less in aqueous iodine than in iodine dissolved in KI. Acceleration depends on the number of inactive molecules activated and always the same fraction of inactive molecules is activated according to Maxwell's rule for the

4

same change of temperature. Hence when initial velocity is correspondingly higher, the number of inactive molecules is smaller and acceleration due to temperature is therefore also smaller.

The photochemical reaction between sodium formate and iodine in presence of a definite quantity of potassium iodide was first investigated by Mukherji and Dhar (*J. Phys. Chem.*, 1929, **33**, 850) but the reaction between aqueous iodine and sodium formate in light remained uninvestigated. The relation between intensity and velocity for this reaction was studied by Dhar and Bhattacharya (*J. Indian Chem. Soc.*, 1929, **6**, 475) but they did not avoid the presence of potassium iodide. They showed that the relation between intensity and velocity may be direct, less than direct or greater than direct depending on the amount of photochemical acceleration over the reaction.

In a previous paper (Bhagwat, *J. Indian Chem. Soc.*, 1934, **11**, 443), it has been shown that photochemical acceleration is a function of inactive molecules existing in the reacting system at the time of activation by light and that true photochemical reactions must always show a relationship which is less than direct and can never show a relationship greater than unity. The results obtained in the present investigation confirm the above conclusion (*cf.*Bhagwat, *J. Indian Chem. Soc.*, 1933, **10**, 649) and other numerous reactions : it is also confirmed in the present reaction between sodium formate and aqueous iodine with and without the addition of various salts. Results are shown in the following tables.

TABLE III.

Reaction in absence of potassium iodide.

Conc. of $I_2 = 0.00123N$. Conc. of $HCOONa = 0.9252$ g. per litre. In all cases 2g. of the salt are added to 100 c.c. of the mixture.

Temp.	Salt.	Dark K_1	Distance from source	True K_1 in light.	Ratio of intensities.	Ratio of velocities.	
28°	Nil	0.0095	0.5 metre	. 0.0035	4	$\frac{0.0035}{0.0022}$	$= 1.6$
			1	0.0022	—	—	
			2	0.0010	16	$\frac{0.0031}{0.0010}$	$= 3.5$
28°	KBr	0.0047	0.5	0.0031	9	$\frac{0.0031}{0.0008}$	$= 3.9$
			1.5	0.0008	—	—	
26°	KCl	0.00366	0.5	0.00161	4	$\frac{0.00161}{0.00098}$	$= 1.6$
			1	0.00098	—	—	
			2	0.00054	16	$\frac{0.00161}{0.00054}$	$= 3.0$
25.2°	NH$_4$Cl	0.0034	2	0.00020	4	$\frac{0.00040}{0.00020}$	$= 2$
			1	0.00040	—	—	

TABLE IV.

Reaction in presence of potassium iodide.

Conc. of $I_2 = N/21\cdot55$. Conc. of $KI = 51\cdot7181$ g. per litre. Conc. of $HCOONa = 32$ g. per litre. In all cases 2 g. of the salt are added to 100 c.c. of the mixture.

Temp.	Salt.	Dark K_1.	Distance from source.	True K_1 in light.	Ratio of intensities.	Ratio of velocities.
24°	Nil	0·0055	1 metre	0·00080	4	$\dfrac{0\cdot00080}{0\cdot00040} = 2$
			2	0·00040	—	—
25°	KBr	0·0061	0·5	0·00060	4	$\dfrac{0\cdot00060}{0\cdot00035} = 1\cdot75$
			1	0·00035	—	—
			2	0·00020	16	$\dfrac{0\cdot00060}{0\cdot00020} = 3$
24°	NaBr	0·0059	0·5	0·00085	4	$\dfrac{0\cdot00085}{0\cdot00060} = 1\cdot41$
			1	0·00060	—	—
			2	0·00030	16	$\dfrac{0\cdot00085}{0\cdot00030} = 2\cdot8_3$
26°	NaI	0·00132	1	0·00030		$\dfrac{0\cdot00030}{0\cdot00016} = 1\cdot9$
			2	0·00016	—	—
24·2°	NH₄I	0·00132	1	0·00013	4	$\dfrac{0\cdot00013}{0\cdot00007} = 1\cdot9$
			2	0·00007	—	—

All these results point out that even in presence of potassium iodide and other salts, when the reaction is highly retarded, the relation between intensity and velocity never exceeds unity but it always remains appreciably lower.

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PHYSICAL CHEMISTRY OF RESIN SOLUTIONS. PART I. ANOMALOUS SOLUBILITY OF SHELLAC AND OTHER RESINS IN ORGANIC SOLVENTS.

By Santi Ranjan Palit.

Influence of water and other polar helpers on the shellac-acetone system has been investigated on a quantitative basis; wide discrepancies among the solubility values as reported by different workers have been attributed to the presence of minute traces of moisture either in solutes or in solvents. Many other solubility peculiarities of resins have also been attributed to same or similar cause

Solubility of resins, in particular, in different solvents presents some apparently puzzling aspects which have scarcely any analogue in the case of non-resins. Thus we find that (a) when the solution of a resin in an organic solvent, such as shellac in acetone, pontianak or manila copal in alcohol, or the soft resin of shellac in ether, is diluted with the same solvent, turbidity resulting in the precipitation of the resin occurs (cf. Coffignier, "Varnishes, Their Chemistry and Manufacture", pp. 43, 47). (b) Secondly, when a given quantity of any solvent has dissolved sufficient quantity of a resin added to it and refuses to dissolve more (i.e. apparently saturated), further solution may be effected by addition of more resin. This is generally explained as a colloidal phenomenon according to "Bodenkörperregel" of Wo. Ostwald and Von Buzagh ("Colloid Systems", 1937, p. 251) applicable to colloids. Barry ("Natural Varnish Resins", 1932, p. 18) also refers to such observations and ascribes them to colloidal effects. (c) Thirdly, it has been observed that while it is difficult to prepare a dilute solution (say 5% of shellac in acetone) even by boiling, a concentrated solution (30 or 40%) can be prepared without any difficulty. These types of anomalous solubilities of resins are well known to practical varnish manufacturers, although the real mechanism of these has not yet been clarified. The present investigation is directed to elucidate such behaviours and to offer explanation, if possible

As to (a) and (c) Tschirch and Stock ("Die Harze", 1932, Band I, pp. 111, 147) remark that "Sehr haufig beobachtet man namlich bei Harzen die Erscheinung, dass sich des ganze Extreckt Z.B. in wenig. Äther löst, dass aber bei Zusatz von mehr Lösungsmittel ein Teil wieder ausfallt. Hat nun der ein Beobachter wenig Äther für den Versuch verwendet, so wird er die Angabe machen : das Harz ist schon in wenig Äther vollständig löslich " hat der andere Beobachter aber von vornherem viel Äther benutzt, so wird er bei dem gleichen Harze die Angabe registrieren : das Harze ist selbst in viel Äther nicht vollständig löslich." They explain this on the

assumption that resins are usually, mixtures of which the insoluble constituents dissolve in a concentrated solution of other soluble resins present. This assumption cannot, however, be generally justified in view of the fact that many highly purified resins, which are known to consist of single molecular species, also exhibit such behaviours and also in view of the observation that the precipitate formed by dilution with the solvent and the residue remaining undissolved, usually contain all the constituents individually. In regard to (c), Drummond (*J. Oil & Col. Chem. Assoc.*, 1925, **8**, 64) explains the mutual solubility relationship on consideration of a solution of an organic liquid in the resin. But such a view does not seem to be probable from our general experience in solubility. Mardles (*J. Soc. Chem. Ind.*, 1933, **42**, 135) observed that not only with cellulose acetate but also with resin " a liquid appears to be a better solvent at higher concentrations " and thus supports Livache and McIntosh (" Manufacture of Varnishes ", 1911, Vol. III, p. 359) that " a concentrated copal solution is often precipitated by adding more of the solvent." Mardles suggests that under such conditions a portion of the colloid is not actually dissolved but simply remains dispersed in a relatively coarse manner. Garder and Harris (*Ind. Eng. Chem. Anal Ed.*, 1934, **6**, 400) observe that for resins " the solute constituents have a tendency to carry into solution material which otherwise remains insoluble in a suspended or colloid state ".

From thermodynamical considerations it is easy to show that if a solute lowers the vapour pressure of a solvent, dilution of the system by the same solvent cannot lead to the precipitation of the solute. Since it has been observed by the author that in these solutions there is always a lowering of vapour pressure of the solvent (determined by boiling point method in Cottrell's apparatus) it is quite likely that the system considered is not purely a simple two-component system, but there may be complexities present which are responsible for these peculiar behaviours. This idea is corroborated by the fact that the anhydrous resin is not soluble in the pure dry solvent and is only soluble when a small quantity of water is present. The presence of ' polar helpers ' necessary for effecting solution has already been observed in many other systems by workers in other fields. Thus, Holmes and Maxson ("Colloid Symposium Monograph", 1928. Vol. V, p. 287) found it necessary to add traces of moisture to dissolve dry sodium stearate and palmitate in hot turpentine, and Faensteiner for barium oleate in a mixture of dry benzene and absolute alcohol (*vide*, Holmes, " Introductory Colloid Chemistry", 1934, p. 100). Even in oil varnishes the addition of a small quantity of hydroxylic compounds has been found to be helpful to prevent gelling, technically known as ' livering ' of varnishes.

It has, therefore, been thought desirable to assess the rôle of water and other helpers in such systems in a quantitative way and in the present paper the shellac-acetone system has been used throughout because the anomalous effects described herein are all readily observable and easily reproducible in this single system.

EXPERIMENTAL.

A. Influence of Water on the Shellac-acetone System.

Influence on Solubility.—Dewaxed lemon shellac (20 g.) was treated with 100 c.c. of acetone in stoppered conical flasks and warmed on a water-bath till clear solution was effected. This was then set aside for 24 hours. A jelly-like mass of shellac separated out and the supernatant liquid was decanted through a dry filter paper. 2 C.c. portions of this solution after addition of measured quantities of water from a microburette were treated with dry acetone from a burette until precipitation of shellac just commenced, which could be easily ascertained if the solutions were viewed against a dark background with lateral illumination. Results given in Table I show absence of any precipitation in presence of sufficient concentration of water in the system.

TABLE I.

Volume of shellac solution used = 2 c.c.

Water added (c.c.) ...	0·00	0·01	0·02	0·04	0·05	0 06	0 08	0·10
Precipitating vol. of acetone (c.c.) ...	1 7	2·3	3·8	7·9	10·1	19·7	completely miscible	

It is evident that the solubility of shellac in acetone depends largely on the concentration of water. So the solubility of shellac has a meaning only with reference to the concentration of water present in the system.

This aspect of the question was further investigated by determination of the solubility of dry shellac in acetone. As it is difficult to desiccate shellac absolutely free from moisture, the hard resin constituent of shellac was used in such experiments. Dewaxed shellac mixed up with coarse sand was repeatedly extracted with ordinary ether. The soft resin portion, which is soluble in moist ether, was removed by solution and the hard resin left (mixed with sand) was repeatedly washed with anhydrous ether and dried. This was then dissolved in absolute alcohol, precipitated out by dry ether, washed with ether free from alcohol and dried again in a current of warm air. This hard resin (also called pure resin, Reinharz, or α-lac) shows a solubility of

o·71 g./100 g. of acetone when 1 g. of it is boiled with 10 c.c. of acetone and set aside for some time.   This insignificant solubility is perhaps due to a trace of moisture still left unremoved in the resin.

Similar phenomenon has also been observed with the soft resin of shellac in ether and also in that of pontianac in alcohol.

Influence on Gel Formation.—20 G. of the same shellac were treated as before, 50 c c. of acetone were added and the changes towards gel formation observed with addition of increasing amount of water.   Results are represented in Table II.

TABLE II.

Shellac used = 20 g.   Acetone added = 50 c.c.

Water added.	Observations.
0·0 c.c.	Swelling of solid with a slightly turbid solution.
0·1	A non-homogeneous gel with solids admixed with a supernatant solution.
0·2	A homogeneous gel with a small quantity of supernatant solution.
0·3	A completely homogeneous non-flowing stiff gel.
0·5	A homogeneous viscid treacle-like liquid
1·0	A free-flowing slightly viscous solution.
2·0	A free-flowing homogeneous solution

Table II clearly brings out the effect of water on the process of gel formation and shows that even a slight change in the concentration of moisture may sometimes convert a gel to a free-flowing liquid.   (This corresponds to the lightly shaded portion in the three component diagram, *vice infra*).   The addition of water obviously reduces the viscosity of the solution.

B.   *Influence of Various Foreign Substances on Solubility.*

It has been observed qualitatively by many workers that water is not the only polar helper and, in fact, any polar compound like alcohol, glycol, etc., functions in a similar way.   Hence the influence of all hydroxylic and carboxylic compounds as helpers, as well as of hydrocarbons like benzene, toluene, *cyclo*hexane, has been investigated in a quantitative way.   Half a gram of dewaxed shellac (dried in vacuum at 42° and stored in a vacuum desiccator over sulphuric acid) was kept with 10 c.c. of dry acetone in loosely stoppered thick-walled pyrex test-tubes, partly immersed in a thermostat at 50°.   This

proportion of shellac to acetone was chosen as the saturated solution had no tendency towards gel formation. Gradually increasing quantities of different liquids (up to 4 c.c. in steps of 0·02 c.c.) were run into the test tubes from a microburette until the shellac completely dissolved and the solution remained clear on cooling to room temperature (27°). Experiments were conducted in duplicate and the results are summarised in Table III.

TABLE III.

Substance.	Amount necessary per 10 c.c. acetone.		Substance.	Amount necessary per 10 c.c. acetone.	
	G.	G. mol.		G.	G. mol.
1. Water	0·53	0·029	12. Xylene	No action	—
2. Methyl alcohol	1·12	0·035	13. Petroleum ether	Do	—
3. Ethyl alcohol	1·47	0·032	14. Formic acid	0·62	0·014
4 n-Propyl alcohol	1·27	0·021	15. Acetic acid	2·20	0·030
5. n-Butyl alcohol	1·68	0·023	16. Propionic acid	2·54	0 034
6 Amyl alcohol	2·36	0·026	17 Lactic acid	0·69	0·0077
7. Benzyl alcohol	1·69	0·015	18. Diethyl ether	No action	—
8. Glycol	0·903	0·014	19. Chloroform	Do	—
9. Glycerol	Immiscible with acetone	—	20 Carbon tetrachloride	Do	—
			21 *Cyclo*hexane	Do	—
10. Benzene	No action	—	22. Methyl ethyl ketone	Do	—
11. Toluene	Do	—	23. Ethyl acetate	Do	—

It should be noted that only polar substances like alcohol, acids, etc., serve as helpers in such solution process but the hydrocarbons, ethers, ketones, etc. are without any effect. It is remarkable that lactic acid, which is both an acid and an alcohol, is the most powerful agent in causing such solutions. In the light of these observations the cause of anomalies among the values of solubility observed by different workers is thus not difficult to foresee. The fact that high molecular weight compounds like resins, nitrocellulose, etc. are sometimes more easily soluble in commercial than in pure solvents can also be easily understood from this.

DISCUSSION.

These observations may be understood in the light of current conceptions regarding solvation of large molecules (Sheppard, Carver and

Houck, "Colloid Symposium Monograph," Vol. V. p. 243; Hildebrand, "Solubility", Chapters IV, V, and VI) which have been succesfully applied in a parallel case *viz.* in nitrocellulose which dissolves in a mixture of alcohol and ether but in none of the solvents singly.

There are reasons to believe that large molecules of shellac having their molecular weight 1000 may be composed of hetergeneous groups, some of which being hydrophilic may be insoluble in acetone, while others dissolve in it. Consequently the complete molecule cannot pass into solution as a whole. The presence of hydrophilic groups in shellac is indi-cated by the supreme difficulty associated with its complete desiccation due obviously to the great tenacity with which it absorbs and retains moisture. These hydrophilic groups adsorb water molecules from moist acetone with the hydroxyl group of water oriented inwards and presenting the hydrogen atom towards the solvent, which can now easily dissolve the whole molecule of shellac. The forces which bring about the adsorption of solvent molecules on the large stout molecules are quasi-chemical or due to residual affinity which is perhaps dynamic in nature, according to Lang-muir's idea, as described by Hildebrand ("Solubility", Chap. IV). In fact, the process of peptisation is not limited to giant molecules or micelles of colloidal dimensions, but seems to occur in molecules of all sizes and weights, resins being but cases where the mass of peptised molecules lies between 300 and 1000. In the same extended sense, peptisation is occurring in the solution of soap in turpentine, of calcium acetate in alcohol in presence of traces of water.
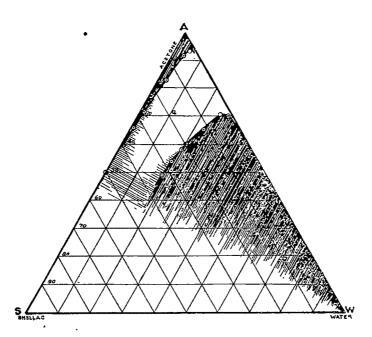
On the basis of this picture, the solubility of shellac in different solvents can be understood. The soft resin of shellac, which contains a preponderance of non-polar groups dissolves in solvents like ether, toluene, esters, etc. more easily if these solvents are moist or contain a small quantity of polar liquids like water, alcohols, etc. which confer upon them a slight degree of polarity. The insolubility of hard resins under the same circumstances may be explained as due to its comparatively large size (mol. wt. about 2000) being composed of a variety of groups of different degrees of polarity. The necessarily low concentration of moisture in most non-polar organic solvents explains the preferential solution of the soft resin constituent of shellac in them. It is quite likely that by adjusting the polarity of the solvent like toluene, acetone, etc. by addition of suitable polar compounds as alcohol, water, acetic acid, etc. the soft resin can be easily dissolved out of shellac leaving the hard resin almost unaffected. A combination of two miscible solvents, one polar and the other non-polar, in suitable proportions may also produce an appropriate solvent for hard resin of

shellac, though they may not be solvents when used singly. Such combinations have been realised experimently, some typical cases being acetone and glycol, methyl acetate and water or glycol, etc.

The swelling of shellac in different non-polar solvents like benzene, ether, etc. is probably due to the solvation of the non-polar part by the solvent. That partial solvation of the resin molecule occurs even with non-solvents, is plainly shown by warming pure shellac resin with dry acetone. The glassy (vitreous) resin swells to a loose, fluffy mass which does not go into solution, but on addition of a few drops of water, swells to a homogeneous gel and quickly dissolves in the solvent.

The significance of such phenomena appears to be far-reaching and throws light on the question of the ultimate molecular structure of resin and the solvation of its atomic groups. The 'blushing' of shellac films and the comparatively low water resistance of ordinary shellac mouldings, for example, may be ascribed to these hydrophilic groups. Judging from this we should naturally expect that combination with a polar substance having less affinity for water will make shellac comparatively resistant to water. Addition of urea has been recommended (Venugopalan, Ranganathan and Aldis, *Synthetic and Applied Finishes*, 1934, 5, 161) for non-blushing shellac-spirit varnish which undoubtedly acts by being adsorbed and thus covering the hydrophilic carboxyl groups. Cellulose is perhaps the best to this requirement and in fact it has been observed that mouldings obtained from well dried shellac with cellulose fibre as filler in the form of blotting paper, cotton, paper-pulp etc. are much stronger and more water-resistant. The solubilisation of shellac in drying oil by acetylation or by heating with glycerine in the oil mixture can also be understood from the above discussion. Britton (*J. Oil. Col. Chem. Assoc.*, 1928, 2, 325) observed that on dialysing a rosin oil-varnish through semipermeable septa, the rosin diffuses out but, after some time it separates out of the dialysate. Britton *(loc. cit.)*, however, explains it as due to an allotropic transformation of rosin but this can also be explained in the light of our present observations. The solvated resin molecules which first diffuse out into the oil, slowly loose their adsorbed polar groups as the equilibrium is certainly disturbed in the new less polar environment and thus the resin gets finally precipitated.

The dissolution of shellac in acetone is thus a process in which water, though unsuspected, plays a very important rôle and is in fact essential to its solubility. Hence in such cases what we are dealing with is not a two-component system of the solvent and the solute alone but a three-component one, including the traces of water whose rôle cannot be exaggerated.

Fig. 1

Mutual solubility relationship among shellac, acetone and water.

A three-component figure represented on an equilateral triangle has therefore been presented to give a complete picture of the mutual solubility relations, determined for a dry sample of dewaxed lemon shellac at a temperature of 27° (Fig. 1). Compositions corresponding to the blank portion, '*a*' show complete solubility, whereas deeply shaded portions are heterogeneous. Lightly shaded portions signify the region of gel formation. From this it will also be observed that to prepare a solution of 2·0 g. of shellac per 100 g. of acetone at room temperature, moisture, more than 200% of the weight of shellac, is necessary, whereas for a 33·3% solution, moisture equivalent to only 3% of the weight of shellac is quite sufficient—a fact which probably explains the anomalies in (a) and (c).

CONCLUSIONS.

The results obtained indicate that the wide discrepancies among the solubility values of resins reported by different workers is primarily due

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to the effect of the presence of small quantities of unsuspected impurities, very often traces of moisture, present in the resin in the solvent or in both. ·The anomalous solubility data obtained by using different quantities of the same resin can also have an explanation on this basis.

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IRON AND MANGANESE REQUIREMENTS OF THE HUMAN ADULT.

By K. P. Basu and M. C. Malakar.

The average daily excretion of iron in those cases in which the experimental subject (two adult men) were nearly in iron equilibrium was 10·2 mg. and 8·6 mg respectively. Urinary iron excretions varied between 1·5 and 0·783 mg. per day.

Addition of calcium in the form of milk had no effect on iron retentions. The amount of so-called available iron in the food as measured by the dipyridyl method bore no relation to the amount absorbed.

Manganese was almost entirely eliminated along with the faeces The average requirement for balance was 3·7, 3·8 and 5·5 mg. respectively in the case of three adult men.

Experiments on the amount of food-iron necessary for the maintenance of equilibrium have been very few in number. Sherman ("Chemistry of Food and Nutrition," 1937) summarises the data on iron requirement of normal human adults investigated in twenty-one cases and suggests that an average intake of about 8 mg. of iron per day is needed for men and women. It is necessary to study iron metabolism in more subjects before definite conclusions can be drawn with regard to iron requirements. It will also be interesting to investigate if there is a relation between the intake of available iron as measured by the dipyridyl method (Elvehjem et al, J. Biol. Chem., 1933, 103, 61) and the amount of iron utilised by human beings.

Manganese is a normal constituent of practically all tissues and plays specific rôles in metabolism. Investigations from McCollum's laboratory (Orent and McCollum, J. Biol. Chem., 1931, 92, 651) show that manganese is an essential element from the stand-point of nutrition. It has been generally held that the amounts of manganese required per day are so small that an ordinary diet cannot be deficient in this element. It is, however, desirable to determine the minimal amount of manganese in the daily diet necessary for the maintenance of equilibrium in man. No studies in manganese requirements of human adults appear to have been undertaken.

EXPERIMENTAL.

Experiments on iron metabolism were performed on two healthy adults (men) S. N. D. (24 years, weighing 49 kilos) and U. C. S. (30 years, weighing 48 kilos). Experiments on manganese requirements were performed on the same two individuals and also on G. C. N. (19 years,

weighing 49 kilos). They lived with and were kept under the strict supervision of one of the authors (M.C.M.). They too realised the importance of the investigations, co operated whole-heartedly in the work, led a strictly disciplined life during the periods of experiment and took nothing but the weighed amounts of food daily supplied to them. The composition of the diets is indicated later. In each series of experiments the cereal and pulse were taken from the same stock every day ; aliquots of vegetables, fish and milk taken daily were pooled for analysis. With one particular diet the experimental subjects were daily given carefully weighed diets which they consumed *in toto* in two portions. In certain experiments only distilled water was used for drinking and cooking purposes. In those cases where tap water was employed the iron content of the water was taken into consideration. Tap water does not contain manganese in appreciable amounts. Each diet was taken for 6 or 9 days ; the first three days were considered as a preliminary period to avoid any effect produced by the previous diet. Urine was collected quantitatively for 24 hour periods and the faeces for three days were collected together since the daily dry weight of the faeces was found to vary considerably. Faeces were marked by carmine.

After this six or nine day period on a particular diet, the effect of supplementing the diet with 275 c.c. of milk daily was observed for 6 days, urine being daily collected and analysed, while faeces for three day periods were collected together.

Since iron metabolism was being studied special precautions were taken. A special glass room was constructed in the laboratory where all the analyses of iron were performed. All possible sources of contamination with iron were avoided. Tripod stands and the wires in the fireclay triangles were made of copper. Aluminium utensils were used for cooking purposes and excrete were collected in aluminium vessels and dried over an aluminium dish in a room specially made to avoid contamination with iron.

Total iron was estimated by the thiocyanate method (Farrar, *J. Biol. Chem.*, 1935, **110**, 685) and the available iron in foodstuffs by the aa'-dipyridyl method of Hill (*Proc. Roy. Soc.*, 1930, **B, 107**, 207) developed by Elvehjem, Hart and Sherman (*J. Biol. Chem.*, 1933, **103**, 61).

Manganese was estimated by the method of Skinner and Peterson (*J. Biol. Chem.*, 1930, **88**, 347). Only traces of manganese were eliminated in urine.

All the experimental subjects were in nitrogen balance on the diets employed.

RESULTS.

The first experiment was performed on S. N. D. who took polished rice (550 g.), lentil (60 g.), vegetables (200 g.), fish (*Labeo rohita*) (65 g.), butter-fat (30 g.) and distilled water *ad libitum* per day. The diet was taken for 12 days, 275 c.c. of milk being added during the last 6 days. First three days and also the first three days of the milk diet were taken as preliminary periods and no collections were made on these days. Iron and manganese metabolism on this diet is indicated in Table I. In this and in the following tables figures of intake and output represent daily averages.

TABLE I.

Experimental subject: S. N. D.

	Iron metabolism.						Manganese metabolism.		
Day of expt.	Total dietary iron.	Available dietary iron.	Urinary iron.	Faecal iron.	Total iron output.	Balance.	Total dietary Mn.	Faecal Mn.	Balance.
4th			1·5 mg.						
5th			1·6						
6th			1·5						
Mean	14·0 mg.	7·9 mg.	1·5	9·3 mg.	10·8 mg	3 2 mg.	6·9 mg.	6·0 mg.	0·9 mg.
(Diet & milk)									
10th			1·7						
11th			1·4						
12th			1·3						
Mean	14·54	7·9	1·5	9·3	10·8	3·7	6·9	5·3	1·6

The second experiment was also performed on S. N. D. who was daily given highly polished rice (550 g.) to diminish the intake of iron, lentil (60 g.), vegetables (200 g), fish (*Labeo rohita*) (50 g.), sugar (100 g.), mustard oil (30 g.) and distilled water *ad libitum*. The diet was taken for 12 days, 275 c.c. of milk being added during the last 6 days. The first three days were taken as a preliminary period. The iron and manganese metabolism on this diet is indicated in Table II.

TABLE II.

Experimental subject : S. N. D.

Day of expt.	Iron metabolism.						Manganese metabolism.		
	Total dietary iron.	Available dietary iron.	Urinary iron.	Faecal iron.	Total iron output.	Balance.	Total dietary Mn.	Faecal Mn.	Balance.
4th			1·0 mg.						
5th			1·6						
6th			1·0						
Mean	9·3 mg.	6·6 mg.	1·2	11·7 mg.	12·9 mg.	−3 9 mg.	4·2 mg.	3·8 mg.	0·4 mg.
(Diet & milk)									
7th			0·8						
8th			0·9						
9th			0·7						
Mean	9·5	6·6	0·8	9·6	10 4	−0 9	4·2	3·3	0·9
(Diet & milk)									
10th			0·8						
11th			0·8						
12th			0·8						
Mean	9·5	6·6	0·8	8·0	8·8	+0 7	4·2	4 1	0·1

The third experiment was performed on U. C. S. The composition of the diet was as follows :—Rice (coarse) (600 g.), lentil (60 g.), vegetables (200 g.), fish (*Labeo rohita*) (70 g.), mustard oil (30 g.), sugar (50 g.) and tap water. The diet was taken for 12 days, 275 c.c. of milk being added during the last 6 days. First three days were taken as a preliminary period. Iron and manganese metabolism of this diet is indicated in Table III.

TABLE III.

Experimental subject : U. C. S.

Day of expt.	Iron metabolism.						Manganese metabolism.		
	Total dietary iron.	Available dietary iron.	Urinary iron.	Faecal iron.	Total iron output.	Balance.	Total dietary Mn.	Faecal Mn.	Balance.
4th			1·04 mg.						
5th			1·2						
6th			1·2						
Mean	19·56 mg.	15·36 mg.	1·14	7·77 mg.	8·91 mg.	10·65 mg.	6·6 mg.	4·9 mg.	1·7 mg
(Diet & milk)									
7th			1·12						
8th			1 28						
9th			1·05						
Mean	20·1	15·36	1·15	7·21	8·36	11·74	6·6	6·1	0·5
(Diet & milk)									
10th			0·75						
11th			1·02						
12th			1·0						
Mean	20·1	15·36	0·92	7·5	8·4	11·68	6·6	·5·4	1 2

The fourth experiment was also performed on U. C. S. He was daily given whole wheat (500 g.), horse gram (70 g.), vegetables (180 g.), butter-fat (30 g.), sugar (50 g.) and tap water. The diet was taken for fifteen days 275 c.c. of milk being given during the last 6 days. First three days were taken as a preliminary period. The iron and manganese metabolism on this diet is indicated in Table IV.

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TABLE IV.

Experimental subject: U.C.S.

Day of expt.	Iron metabolism						Manganese metabolism		
	Total dietary iron.	Available dietary iron.	Urinary iron.	Faecal iron.	Total iron output.	Balance.	Total dietary Mn.	Faecal Mn.	Balance
4th			·6 mg.						
5th			0·79						
6th			0·9[]						
Mean	25·03 mg.	10·02 mg.	0·78	17·1 mg.	17·88 mg.	7·15 mg.	22·5mg.	12·0 mg.	10·5 mg.
7th			0·85						
8th			0·80						
9th			0·85						
Mean	25·03	10·02	0·83	16·99	17·82	7·21	22·5	13·9	8·6
(Diet & milk)									
10th			0·78						
11th			0·80						
12th			0·87						
Mean	25·58	10·02	0·82	16·64	17·45	8·12	22·5	13·6	8·9
(Diet & milk)									
13th			0·86						
14th			0·77						
15th			0·84						
Mean	25·58	10·02	0·82	15·09	15·9	9·6	22·5	10·0	11·6

The fifth experiment in which only manganese metabolism was studied was performed on G.C.N. He was daily given polished rice (550 g.), lentil (60 g.), vegetables, (200 g.), fish (*Labeo rohita*) (70 g.), mustard oil (30 g.) and distilled water *ad libitum*. The diet was taken for 15 days, 275 c.c. of milk being added during the last 6 days. First three days were taken as preliminary period. Manganese metabolism on this diet is indicated in Table V.

TABLE V.

Experimental subject : G.C.N.

Day of expt.	Total dietary manganese.	Urinary manganese.	Faecal manganese.	Balance.
4th		Trace		
5th		,,		
6th		,,		
Mean	4·5 mg.	,,	3·7 mg.	0·8 mg.
7th		,,		
8th		,,		
9th		,,		
Mean	4·5	,,	3·3	1·2
(Diet & milk)				
10th		,,		
11th		,,		
12th		,,		
Mean	4·5	,,	4·1	0·4
(Diet & milk)				
13th		,,		
14th		,,		
15th		,,		
Mean	4·5	,,	4·2	0·3

The sixth experiment on manganese metabolism was also performed on G.C.N. He was daily given whole wheat (550 g.), horse gram (70 g.), vegetables (180 g.), butter-fat (30 g.), sugar (60 g.) and tap water. The diet was taken for 15 days, 275 c.c. of milk being added during the last 6 days. First three days were taken as a preliminary period. Manganese metabolism on this diet is indicated in Table VI.

TABLE VI.

Experimental subject: G.C.N.

Day of expt.	Total dietary manganese	Urinary manganese	Faecal manganese.	Balance.
4th		Trace		
5th		,,		
6th		,,		
Mean	21·4 mg.	,,	14·9 mg.	6 5 mg.
7th		,,		
8th		,,		
9th		,,		
Mean	21·4	,,	16·9	4·5
(Diet & milk)				
10th		,,		
11th		,,		
12th		,,		
Mean	21·4	,,	19·9	1·5
(Diet & milk)				
13th		,,		
14th		,,		
15th		,,		
Mean	21·4	,,	18·0	3·4

DISCUSSION.

In the following table the iron outputs in those cases in which balance was nearly attained have been collected together.

TABLE VII.

Iron outputs near balance.

Experimental subjects	Iron output near equilibrium.	Mean iron requirement.	Reference to data
S.N.D. (49 kilo)	10·8 mg.		Table I
	10·8		,, ,,
		10·2 mg.	,, ,,
	10·4		,, II
	8·8		,, ,,
U.C.S. (48 kilo)	8·9		Table III
	8·4	8·6	,, ,,
	8·4		,, ,,

The mean iron requirement was thus 10·2 mg. in one case and 8·6 mg. in the other case. The mean of these two results is 9·4 mg., a value which is nearer to the previously recommended value of 10 mg. of Sherman (*loc.cit.*) It would also appear from the data on iron metabolism that the so-called available iron as measured by the αα'-dipyridyl method has very little effect on iron retentions. A reference to the metabolism studies would also show that supplementation with milk and hence with calcium has got little favourable effect on the retention of iron as was observed by Sherman (*loc. cit.*) and by Orlin, Smith and Mendel (*J. Nutrition.*, 1935, **12**, 373).

On wheat diets the manganese intakes were far in excess of requirement while the experimental subjects were nearly in manganese equilibrium on rice diets. It is interesting to note that the whole of the manganese was excreted along with the faeces and only traces could be detected in the urine. The outputs near balance points are indicated below.

TABLE VIII.

Manganese outputs near balance.

Experimental subjects.	Manganese output near equilibrium.	Mean manganese requirement.	Reference to data
S.N.D. (49 kilo)	3·8 mg.		Table II
	3·3	3·7 mg.	,,
	4·1		,,
G.C N. (49 kilo)	3·7		Table V
	3·3	3·8	,,
	4·1		,,
	4·2		,,
U.C.S. (48 kilo)	4·9		Table III
	6·1	5·5	.,
	5·4		,,

The mean manganese requirement for balance is thus 3·7 mg. per day in one case and 3·8 mg. and 5·5 mg. in two other cases. The mean of these values is 4·6 mg. per day. In none of the twenty metabolism experiments recorded in this paper was a negative manganese balance obtained. Milk contains only traces of manganese and its addition to diets does not affect manganese metabolism.

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AN INVESTIGATION ON SOIL AND PEAT HUMIC ACIDS. PART I. ISOLATION AND PURIFICATION OF THE ACIDS.

By G. C. ESH AND S. S. GUHA-SIRCAR.

Two humic acids isolated from two Assam tea soils have been compared with two commercial humic acids isolated from peat in regard to the content of C, H, N, OMe, acetyl and furfural and formaldehyde-yielding groups.

The organic matter of soils and of peat has engaged the attention of the scientific investigators ever since the latter part of the 18th century. Although various theories have been proposed, the origin and the constitution of humic acid are still incompletely understood.

Achard (Crell's *Chem. Ann.*, 1786, **2**, 391) first used the alkali extraction method for isolation of humic acid from peat. Sprengel *(Kastner's A. Ges. Naturalchie*, 1826, **8**, 145) described the preparation and properties of humic acid and its salts for the first time.

Seyler (*Z. physiol. Chem.*, 1889, **13**, 647) studied both artificial and natural humic acids. He distinguished these groups of humus substances on the basis of their solubilities in alkali and alcohol, and concluded that in the natural decomposition of plant residues, lignin complexes take active part in the production of humic acid.

By applying modern physicochemical methods of investigations, Odèn (*Koll-Chem. Beihefte*, 1919, **11**, 75) tried to give an idea about the origin and chemistry of various humic acids. He isolated humic acid from peat and soil by treating these first with an acid, washing with water and extracting overnight with $4N$-ammoniacal or sodium hydroxide solution. Sufficient sodium chloride was then added to the alkali solution to make it $2N$. The dark coloured filtrate, obtained after centrifuging, was concentrated, acidified with hydrochloric acid in presence of sodium chloride, centrifuged and washed. This precipitate was treated with alcohol. The alcohol-insoluble portion was called humic acid and the alcohol-soluble portion hymatomalanic acid. He concluded that humus acid and hymatomalanic acid were definite chemical entities. Page (*Agric Sci.*, 1930, **20**, 455) suggested the term humic matter to describe the dark colured high molecular colloidal organic bodies found in soils and composts. He referred to that part of the humic matter, which is soluble in cold weak alkali and is precipitated by acids, as 'humic' acid and the part, insoluble in cold alkali but soluble in hot alkali solution, as 'humin'. Later on Springer, Karrer,

Maliktin and others reported that acetyl bromide is the reagent which can separate lignin and other plant constituents from humic acids. Thus Karrer (*Helv. Chim. Acta*, 1921, **4**, 700) and Groszkopf *(Brennstoff. Chem.*, 1929, **10, 116**, 213) showed that the undecomposed plant constituents which are mixed with humus are easily dissolved by acetyl bromide, while the dark coloured, modified and synthesised complexes remain insoluble. Lignin has also been found to be soluble in this reagent. Springer (*Pflanz, Dung. Bod.*, 1931, **A22**, 135) has demonstrated that the humic acid isolated from soil by means of acetyl bromide contained comparatively large proportion of nitrogen and hence concluded that the soil humus contains both nitrogen-containing and nitrogen-free humic acids. It has been found in this laboratory that the so-called hymatomelanic acid (alcohol-soluble portion of the crude humic acids) both from soil and peat is completely soluble in hot acetyl bromide. All the crude (untreated with alcohol) humic acids, when treated with acetyl bromide in a soxhlet, goes into solution to the extent of 30-35%, while the alcohol-insoluble humic acid is but slightly soluble in the reagent even when treated for a week. Jute lignin, previously isolated in this laboratory, has been subjected to this reagent side by side. Almost the whole of it goes into solution but with much difficulty and in a considerable period of time. Purification of humic acid by this reagent is a very tedious task. However, in view of the fact that all the undecomposed portions of humus are removed by this reagent and that a purer staff is obtained, alcohol-extraction is followed by acetyl bromide extraction in the present investigation.

Up to the end of the 19th century, the origin of the natural humic acids was looked for in the carbohydrate part of the decaying plant materials and wood cellulose was regarded as the precursor of natural humic acid. Fischer and Scharder (*Brennstoff. Chem.*, 1921, **2**, 37 ; 1922, **3**, 65, 341) put forward their lignin theory of the origin of humic acid and of coal, according to which the cellulose is largely destroyed by bacterial decomposition, the lignin fraction being more resistant, remains intact, but during humification it is modified and also possibly polymerised to form humic acid. According to Waksman (*Soil Sci.*, 1932, **34**, 43 ; 1933, **36**, 57) humus formation is largely due to the activities of the micro-organisms which decompose the natural plant and animal residues, like cellulose, hemi-cellulose, pectin etc., but leave the more resistant lignin behind, combined during this decomposition with microbial protein, producing a modified 'lignin-protein complex' which forms the nucleus of the humic acids.

The object of the present investigation is to compare the physical and chemical properties of humic acids obtained from various sources with
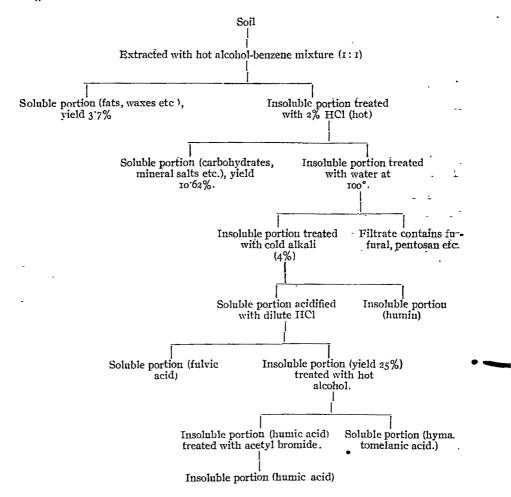
a view to finding out whether they are closely related or otherwise and whether they contain any common molecular framework. For this purpose a comparative study of the nature and relative number of the active groups (hydroxyl and carboxyl), and the products of oxidation etc. is necessary.

EXPERIMENTAL.

Isolation of Humic Acid from Soil.

Like Odèn, Page, Waksman and other earlier investigators and following specially the method of Waksman and Stevens (*Soil Sci.*, 1939, **30**, 97) the soil was first extracted in a Soxhlet apparatus with a mixture of alcohol and benzene (1 : 1) to free it from fats, waxes and resinous matters. After evaporating off the adhering alcohol-benzene, the soil was then treated with ·2% hydrochloric acid at 100° for 1½ hours in order to liberate humic matter combined with calcium, aluminium, iron and other metallic oxides and also to hydrolyse the decomposable carbohydrate (hemicelluloses etc) and the process was repeated thrice when it was supposed to be complete. The soil was then treated with sufficient water at 100° to free it from acid and to remove all the water-soluble products. In order to extract humic matter the soil was then treated with 4% potassium hydroxide solution in the cold and the mixture was kept stirred in a closed vessel for 8-10 hours. The use of ammonia was apparently not advisable for the extraction in view of the investigations of Fuchs and Leopold who showed that ammonia is very strongly adsorbed by humic acid and possibly may also introduce amide groups into the humic acid molecule. The cold alkali extraction was repeated thrice and the clear dark coloured humate solutions were combined, diluted, filtered and the filtrate acidified with dilute hydrochloric acid. The precipitated humic acid was allowed to settle. The clear supernatant liquid was decanted off and the precipitate was shaken up again with fresh water and the process of washing by decantation was continued for 7-8 times within 6-7 days. At the end of this period the acid had a tendency to remain suspended or to pass into a colloidal solution. The acid was then separated by centrifuging. The isolated humic acid was again dissolved in 4% potassium hydroxide solution and precipitated by dilute hydrochloric acid and the washing and centrifuging repeated. The acid was then dried at 80°. The dry acid was next treated with hot alcohol under reflux to separate the alcohol-soluble portion (hymatomelanic acid). The alcohol-insoluble portion was filtered off and dried at 80°. This alcohol-insoluble humic acid was then treated with sufficient amount of acetyl bromide in a specially made all-glass extraction

apparatus at 80-90° for 7-10 days with frequent shaking. The filtered residue was dried at 80° for some time, then washed with ether until free from acetyl bromide and then again dried at 80-85° to a constant weight.

A scheme of the different ways of fractionating the soil organic matter is given below.

Soil
|
Extracted with hot alcohol-benzene mixture (1 : 1)
|
```
Soluble portion (fats, waxes etc ),          Insoluble portion treated
         yield 3·7%                               with 2% HCl (hot)
                                                         |
                        Soluble portion (carbohydrates,    Insoluble portion treated
                           mineral salts etc.), yield         with water at
                                 10·62%.                          100°.
                                                                   |
                                      Insoluble portion treated    · Filtrate contains fur-
                                         with cold alkali            fural, pentosan etc.
                                              (4%)
                                                |
                                   Soluble portion acidified      Insoluble portion
                                       with dilute HCl                (humin)
                                               |
                   Soluble portion (fulvic      Insoluble portion (yield 25%)
                            acid)                    treated with hot
                                                        alcohol.
                                                           |
                        Insoluble portion (humic acid)    Soluble portion (hyma-
                        treated with acetyl bromide.         tomelanic acid.)
                                    |
                       Insoluble portion (humic acid)
```

The commercial humic acids obtained from Messrs Merck and Schuchardt were first dissolved in 4% alkali and then precipitated by dilute hydrochloric acid. Alcohol and acetyl bromide extractions were also done in these cases.

The humic acids thus obtained from four sources, Messrs Merck, Schuchardt and from two Assam soils, were analysed for C, H, N, ash, methoxyl, acetyl etc. The results of analysis are given in Table I.

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TABLE I.

	Alcohol-insoluble humic acids.				Alcohol-soluble hymatomelanic acids.		
	Merck.	Schu.	Derby soil.	Saph. soil.	Merck.	Schu.	Derby soil.
Ash	3%	8 86%	5·2%	7·2%	1·68%	1·45%	4·5%
N	1·6	1·2	1·22	3·6	1·26	0·87	1·05
OMe	2·11	2·55	3·99	5·4	2·31	4·18	4·6
Acetyl	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Carbon	55·5	55·2	54·0	55·12	58·8	57·8	59·2
H	5·2	4·6	5·0	5·63	5·6	5·1	4·51
Furfural-yielding complexes.	Nil	Nil	Traces	Traces	Nil	Nil	Nil
HCHO-yielding group	Nil	Nil	Traces	Traces	Nil	Nil	Nil

The ash in the different humic acid is not negligible. The ash in the peat humic acids (Merck and Schuchardt) was of greyish white colour and was found to contain iron, silica, aluminium, magnesium and traces of copper. But the ash in the soil humic acids was of a reddish brown colour indicating the presence of a high percentage of iron. The alcohol-soluble portions had lower amount of ash. Methoxyl-content in all the humic acids was not very high, while none of the humic acids contained acetyl groups. Barium salts of all the acids were prepared. Equivalent weights were calculated from the percentage of barium. This will be discussed in a separate paper.

TABLE II.

	Acetyl bromide-insoluble humic acid.			
	Merck.	Schuchardt.	Derby soil.	Saphinjuri soil.
Ash	2·09%	5·16%	2·02%	3·5%
N	1·93	1·4	2·8	3·2
C	56·2	56·8	58·3	56·9
H	5·1	4·85	5·2	5·5
OMe	1·79	2·29	3·26	3·8
Acetyl	Nil	Nil	Nil	Nil
HCHO-yielding groups	,,	,,		
Furfural-yielding complexes	,,			

The ash content of all the humic acids has been fairly reduced. With the exception of one, the nitrogen-content has been increased. The methoxyl-contents have been lowered though they are not equal in all cases Some of the previous investigators have found comparatively large amounts of methoxyl in some of the humic acids (*e.g.*, soil and peat); this is due probably to incomplete purification. Though Fuchs and some other investigators have demonstrated the presence of acetyl in soil humic acid, the presence of this group is not noticed in the present work.

With a view to seeing whether the humic acids contain any carbohydrate group (which may have survived the treatment with 2% hydrochloric acid at 100°) one of the substances was distilled with 100 c c. of 12% hydrochloric acid, but the distillate gave only a slight yellowish colouration with phloroglucinol indicating the absence of any appreciable amount of furfural or furfural-yielding complexes.

In order to see whether the humic acid has any formaldehyde-yielding groups (methylenedioxy-) 0·5 g. of the acid was distilled with 100 c.c. of 28% sulphuric acid. 10 C.c. of the distillate were treated with Schryver's reagent; but no appreciable red colour was developed indicating that humic acids either from peat or soil do not contain any formaldehyde yielding groups.

THE EFFECT OF THE INJECTION OF COBRA VENOM ON THE ASCORBIC ACID CONTENT OF DIFFERENT TISSUES OF THE GUINEA-PIG

By A. C. MAJUMDAR.

Injection of cobra venom into guinea-pigs has been found to cause a depletion in the ascorbic acid content of brain, liver, adrenal, kidney and small intestine of guinea-pigs. The spleen is unaffected.

It has been observed that injection of diphtheria toxin causes an appreciable decrease in the vitamin C content of the tissues like adrenal, liver and kidney of guinea-pigs (Ghosh, *J. Indian Chem. Soc.*, 1939, **16**, 241 ; Lyman and King, *J. Pharmacol.*, 1936, **56**, 209 ; Harris, Passmore and Pagel, *Lancet*, 1937, **233**, 183). The administration of different drugs like atophan, quinine, arsenobenzene and poisons like phosphorus (Borselti, *Bull. Soc. Ital. Biol. Sper.*, 1938, **13**, 248; Wullner, *Munch. Med. Woch.*, 1938, **185**, 1785; Karolyi, *Orv. Hetil.*, 1938, **82**, 829; Ryang, *Trans. Soc. Path. Japan*, 1938, **28**, 486; *Nutritional Abstracts*, 1939, **8**, 646) have also been found to cause a reduction in tissue ascorbic acid. The present work was undertaken to investigate the effect of cobra venom on the vitamin C content of the tissues of the guinea-pig.

EXPERIMENTAL.

Male guinea-pigs weighing between 300 and 350 g. were fed on a normal diet of germinated gram and green grass *ad lib.*

Minimum Lethal Dose —The minimum lethal dose (M.L.D.) for the animals was determined by injecting a weighed amount of cobra venom dissolved in normal saline, into the calf muscle of the hind leg of the animal. The dose which caused the death of 50% of the animals injected weighing between 300 and 350 g. within 24 to 48 hours was taken as the M.L.D.

The animals were killed by blowing air into their heart. As soon as the animal was dead tissues like brain, liver, adrenal, kidney, spleen and small intestine were separated and kept in a cold store (4°). They were taken in succession for the estimation of vitamin C.

The Method of Extraction of Ascorbic Acid from the Tissues.

Brain.—The whole of the brain tissue was taken in a glass mortar and was ground well. The minced tissues (2 g.) were weighed on a watch-

glass and were transferred into a mortar with a little sea-sand. 20% Trichloroacetic acid (2 c.c.) was added and the whole material was thoroughly ground. This was transferred to a 25 c.c. measuring cylinder and the volume was made up to 25 c.c. The solution was left to stand for a few minutes when the suspended particles settled to the bottom. The clear liquid at the top was filtered and taken for titration.

Liver.—The method employed was the same as for brain. The tissue (4 g.) was ground with 4 c.c. of 20% trichloroacetic acid and the final volume was made up to 50 c.c. and titrated.

Adrenal.—Both the adrenal glands of the animal were weighed and transferred to a mortar with sea-sand. 20% Trichloroacetic acid (1 c.c) was added and the material extracted as before making up the volume to 20 c.c.

Kidney.—The whole kidney (1.5 g.) was taken with 2 c.c. of trichloroacetic acid. The volume was made up to 20 c.c.

Spleen.—The whole of the spleen was taken with 1 c.c. of trichloroacetic acid and the volume of the extract was adjusted at 20 c.c.

Small Intestine.—The small intestine (4 g.) was taken with 4 c.c. of trichloroacetic acid and treated as before. The final volume was made up to 50 c.c.

Estimation of Vitamin C.

The method of Sen-Gupta and Guha (*J. Indian Chem. Soc.*, 1939, **16**, 547) was employed.

The tissue extracts obtained as above were titrated as quickly as possible against 0·1 c.c. of 2:6-dichlorophenol-indophenol (1 c.c. was equivalent to 0·104 mg. of ascorbic acid). An aliquot part (10 c.c.) of the tissue extract was taken in a flask and the p_H was adjusted to 5·6 by means of NaOH. 2 C.c. of an acetate buffer of the same p_H were added. Fresh cucumber juice was extracted, diluted 3 times and used as the source of ascorbic acid oxidase. The diluted juice (2 c.c.) was added and the mixture was incubated at 37° for half an hour. The volume was then made up to 15 c.c. and this was titrated against 2:6-dichlorophenol-indophenol. In control experiments the same sample of cucumber juice has been found to be entirely devoid of vitamin C before and after incubation and to be particularly rich in the oxidase. The difference between the initial titration value and the titration value obtained after oxidase treatment was taken as the measure of vitamin C.

Effect of Cobra Toxin.

In order to investigate the vitamin C content of the different tissues of guinea-pigs during cobra venom poisoning, $\frac{3}{4}$ M.L.D. of cobra venom was injected and the animal was killed 48 hours after the injection. The values for the ascorbic acid contents of different tissues are recorded in Table II. Similar estimation of vitamin C in different tissues was carried out with control animals which did not receive any cobra venom injection (Table I). Some animals received 1/10 M.L.D. of cobra venom and were killed and the vitamin C content of the tissues was estimated (Table III).

TABLE I.

Ascorbic acid figures of normal control animals.

Serial No.	Body wt.	Ascorbic acid in mg. per g. of					
		Brain.	Liver.	Adrenal.	Kidney	Spleen.	Small intestine.
1	333g.	0·074	0·059	0·450	0·069	...	..
2	318	0·076	0·050	0·440	0·066	0 095	0·074
3	315	0 074	0·053	0·430	0·061	0·150	0·076
4	312	0·072	0·054	0 460	0·059	0·147	0·072
5	324	0·079	0·051	0·426	0·057	0·153	0·074
6	324	0·076	0·050	0·586	0·051	0·146	0·079
	Mean	0·076	0·053	0·465	0·060	0·116	0·075

TABLE II.

Effect of single injection of $\frac{3}{4}$ M.L.D. of cobra venom at a time.

Animals were killed 48 hours after injection.

Serial No.	Body wt.	Ascorbic acid in mg. per g. of					
		Brain.	Liver.	Adrenal.	Kidney.	Spleen.	Small intestine.
1	325g.	0·064	0·043	0·240	0·045	...	...
2	325	0·041	0·044	0·280	0·044	0·118	0·044
3	327	0·065	0·046	0·413	0·051	0·120	0·055
4	335	0·063	0·045	0·386	0·045	0·082	0·050
5	345	0·063	0·036	0·260	0·052	0·120	0·062
6	345	0·059	0·036	0·260	0·055	0·118	0·060
	Mean	0·061	0·041	0·306	0·049	0·116	0·054

TABLE III.

Effect of 1/10 M.L.D. of cobra venom injected at a time.

Animals were killed 48 hours after the injection.

Ascorbic   acid   in   mg.   per   g.   of

Serial No.	Body wt.	Brain.	Liver.	Adrenal.	Kidney.	Spleen.	Small intestine.
1	335g.	0·072	0·041	0·460	0·049	0·151	0·069
2	329	0·067	0·052	0·520	0·054	0·183	0·063
3	322	0·070	0·055	0·458	0·048	0·126	0·065
4	330	0·070	0·043	0·447	0·048	0·090	0·065
	Mean	0·070	0·048	0·473	0·050	0·137	0·066

Tables I, II and III show that 48 hours after the injection of $\frac{3}{4}$ M.L.D of venom, there is an appreciable decrease of vitamin C content of the different tissues. But the decrease was not so much when 1/10 M.L.D was injected. Ascorbic acid content of adrenal gland in the latter case did not decrease at all. It is of interest to note that the vitamin C content of spleen was not diminished either by $\frac{3}{4}$ or 1/10 M.L.D. of cobra venom injection.

Detailed investigations were then carried out to find the effect of fractions of one M.L.D. of cobra venom injected on successive days on the ascorbic acid content of the tissues. Five groups of animals were used. The animals of one group received 1/3 M.L.D. of the venom and were killed after 24 hours and the vitamin C content of the tissues was estimated. The second group received 1/3 M.L.D. on two successive days and was killed on the 3rd day. The third group received 1/3 M.L.D. on three successive days, thus receiving one full M.L.D. in all and was killed on the 4th day. The fourth group received one M.L.D. in one injection and was killed the next day. The fifth group acted as controls not receiving any venom injection, which gave a normal figure for tissue ascorbic acid. The results are given in Tables IV, V, VI, VII and VIII.

TABLE IV.

Effect of single Injection of 1/3 M.L.D. of cobra venom.

Animals were killed 24 hours after injection.

Ascorbic acid in mg. per g. of

Serial No.	Body wt.	Brain.	Liver.	Adrenal.	Kidney.	Small intestine.
1	315g.	0·058	0·042	0·265	0·032	0·053
2	310	0·065	0·052	0·278	0·033	0·053
3	320	0·065	0·050	0·257	0·036	0·062
4	315	0·070	0·053	0·258	0·035	0·058
5	322	0·063	0·052	0·316	0·038	0·057
Mean		0·064	0·050	0·274	0·034	0·057

TABLE V.

Effect of 1/3 M.L.D. injected on two successive days.

Animals were killed on the 3rd day.

Ascorbic acid in mg per g of

Serial No.	Body wt	Brain.	Liver.	Adrenal.	Kidney.	Small intestine.
1	350g.	0·053	0·042	0·204	0·032	0·052
2	320	0·054	0·044	0·196	0·031	0·052
3	315	0 063	0·052	0·205	0·036	0·052
4	312	0·067	0·047	0·261	0·033	0·053
5	320	0·062	0·047	0·244	0·033	0·050
6	330	0·059	0·046	0·210	0·035	0·062
Mean		0·050	0·047	0·220	0·033	0·053

TABLE VI.

Effect of 1/3 M. L. D. injected on three successive days.

Animals were killed on the 4th day.

Ascorbic acid in mg. per g. of

Serial No.	Body wt.	Brain	Liver.	Adrenal.	Kidney.	Small intestine
1	310g.	0·065	0·052	0·220	0·036	0·057
2	315	0·063	0·053	0·270	0 034	0·055
3	300	0·062	0·051	0·226	0·037	0·052
4	312	0·057	0·050	0·263	0·036	0·052
5	335	0·058	0·040	0·271	0·034	0·053
6	325	0·062	0·045	0·289	0·033	0·052
Mean		0·061	0·048	0·257	0·035	0·053

TABLE VII.

Effect of single injection of one full M.L.D.

Animals were killed on the next day when about to die.

Ascorbic acid in mg. per g of

Serial No.	Body wt.	Brain.	Liver.	Adrenal.	Kydney.	Small intestine.
1	350g.	0·062	0·047	0·190	0·032	0·059
2	345	0·056	0·046	0·207	0·033	0·053
3	330	0·054	0·042	0·223	0·031	0·052
4	310	0·055	0·045	0·165	0·030	0·049
5	325	0·055	0·044	0·229	0·032	0·052
Mean		0·057	0·042	0·206	0·032	0·053

TABLE VIII.

Ascorbic acid figures for normal animals.

Ascorbic acid in mg. per g. of
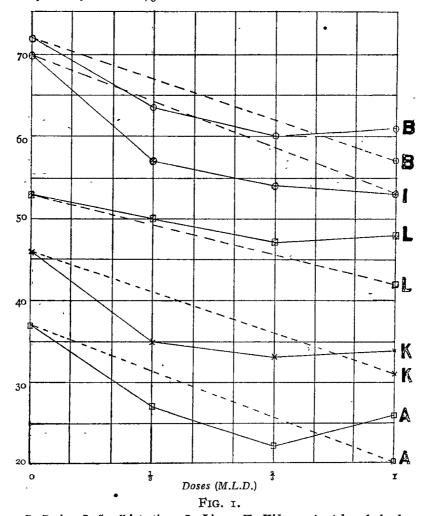
Serial No.	Body wt	Brain.	Liver.	Adrenal	Kidney	Small intestine
1	352g	0·076	0·055	0·431	0·052	0·068
2	345	0·070	0·053	0·406	0·048	0·076
3	315	0·068	0·051	0·353	0 040	0·070
4	310	0·074	0·053	0·324	0·045	0·067
5	335	0·071	0·052	0·364	0·046	0·069
6	342	0·073	0·054	0·367	0·043	0·072
Mean		0·072	0·053	0·370	0·046	0·070

The mean values of the ascorbic acid recorded in the above tables are shown in relation to the varying doses of cobra venom injected in Fig. 1.

DISCUSSION.

Depletion of tissue ascorbic acid in guinea-pigs injected with diphtheria toxin has been investigated by various workers (*loc. cit*). The present investigation shows similar depletion of vitamin C content of tissues like brain, liver, adrenal, kidney and small intestine as a result of the injection of the snake venom. The spleen, however, did not show any reduction in ascorbic acid content. Fig. 1 (dotted lines) shows that for all the tissues

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the decrease of ascorbic acid content is maximum when a full M.L.D. is injected at one time ; in small intestine this maximum decrease is produced even by the injection of $1/3$ M.L.D.

Fig. 1.

B=Brain.   I=Small intestine.   L=Liver.   K=Kidney.   A=Adrenal gland.

The dotted lines indicate the reduction of ascorbic acid value in normal state to that obtained after a single injection of one full minimum lethal dose.

Ascorbic acid in γ (microgram) per g. of tissue. In the case of adrenal gland the value is expressed in mg $\times 10^{-2}$.

It will also be observed (Fig. 1) that the decrease in ascorbic acid values obtained after the injection of $1/3$ M.L.D. on two successive days is greater than that obtained after a single injection of $1/3$ M.LD. But the values obtained after the injection of $1/3$ M.L.D. on three successive days are between the values obtained after a single injection of $1/3$ M.L.D,

and those obtained after two successive injections. These results would seem to indicate that the tissues try to rally their ascorbic acid content during mild intoxication.

It is of interest to investigate the fate of ascorbic acid which disappears and also the nature of the toxic constituent of the venom, which is responsible for causing this disappearance.

With animals receiving the same dose of venom it was observed that in these cases where outward symptoms of toxicity were very pronounced there was a smaller amount of ascorbic acid in the tissues, there was also a considerable hypertrophy of the adrenal gland, the gall bladder was full of bile, and the small intestine was congested with blood, whereas this occurred to a lesser extent in animals which showed less pronounced symptoms of toxicity. It is possible that in the former cases the venom prevents the flow of bile to a greater extent, which might have detoxicated the venom.

My best thanks are due to Dr. J. C. Ray, Dr. B. C. Guha and Dr. B. N. Ghosh for their kind advice.

MECHANISM OF THE MICROBIOLOGICAL OXIDATION OF AMMONIA. PART III.

By G. Gopala Rao and W. V. Sundara Rao.

In this paper evidence is presented to show that the organisms of Winogradsky are mostly responsible for nitrification in the soil It is emphasised here that autotrophic rganisms can flourish well in the presence of organic materials, if in the same medium heterotrophic organisms capable of acting on the particular organic substance are also present.

It was Winogradsky who first isolated in pure culture the nitrifying organisms, the *Nitrosomonas* and the *Nitrosococcus*, autotrophic organisms, which can oxidise ammonia to nitrite. Winogradsky (*Ann. Inst. Pasteur*, 1890, **4**, 213, 215; 1891, **5**, 92, 571) showed that soluble organic matter is very toxic to the growth and respiration of the bacteria. The bacteria are highly specific and act only on one substrate, namely ammonia, oxidising it to nitrite in the presence of atmospheric oxygen and fixing at the same time carbon dioxide into materials necessary for cell growth.

Winogradsky and Omeliansky (*Centrl. Bakt.*, 1899, **5**, 338, 377, 429) further showed that glucose, peptone, asparagine, glycerol and urea are toxic to the organism in concentrations of 0·2 to 1% in liquid cultures. Since this classical work of Winogradsky, the influence of organic substances on nitrifying bacteria has been the subject of investigation by numerous workers If organic substances in low concentrations prove toxic to the nitrifying organisms, knowing that soil contains many types of organic materials, there arises the important question, how can the nitrification in soil be explained? Further we know that nitrification is also very intense in sewage filters and the so-called nitre beds. To explain this three possible avenues have been explored by previous investigators.

It is possible that the organisms isolated by Winogradsky are not the organisms responsible for bringing about nitrification in the soil There may be other species of nitrifying organisms in the soil which either tolerate organic matter, or which actually require organic matter for their growth. Fremlin (*J. Hygiene*, 1903, **3**, 364; 1930, **29**, 236) reported the isolation of a nitrite-forming organism which is capable of growing in media containing organic compounds. Mishustin (*Ber. Bact. Agron. Sta. Moskau*, 1926, **24**, 189) found two spore-forming bacteria capable of producing nitrites in media containing organic nitrogenous compounds but not in inorganic media containing ammonium salts. Runov (*Centrl. Bakt.*, 1928, **7**, 193)

reported two species of bacteria, one of them produced nitrites from organic nitrogenous compounds and the other from ammonia in the presence of organic substances Neither organism grew on Winogradsky's medium and the author concluded that there are many bacteria in nature capable of forming nitrites in media containing various organic substances. Joshi (*Mem. Dept. Agrl. India, Bact. Series*, 1915, No. 3, p. 85) reported a new nitrite-forming organism. Recently Cutler and Mukherjee (*Proc. Roy. Soc.*, 1931, **B**, **108**, 384) reported four species of soil micro-organisms differing completely from the autotrophic organisms of Winogradsky, not only morphologically but also in that they need organic matter. Referring to this work Russell ("Soil Conditions and Plant Growth", London, 1932, p. 331) states, "There seems little doubt that these are the organisms operative in sewage filters, intensive nitre beds and soils containing much organic matter." Cutler and Mukherjee first found these bacteria in the affluent from a beet sugar factory but have since shown that they are widely distributed in soil. It must, however, be said that the amount of nitrites produced by these organisms are very small, the maximum amount of nitrite nitrogen ever formed being only 3·2 parts per million. Even this tends to disappear in the later stages of the experiment. The Winogradsky organisms can produce under favourable conditions, enormous quantities of nitrite, as much as 200 mg. per liter in a few weeks of incubation Regarding the work of Runov and Cutler and Mukherjee, Boltjes (*Archiv Microbiol.*, 1935, **6**, 79) states, "It may be said that one cannot be absolutely certain whether the traces of nitrites obtained by them were really produced by the oxidation of ammonia and not from the absorption of traces of oxides of nitrogen present in the laboratory atmosphere, or more likely through reduction of nitrates." In any case the amount of nitrites obtained by these workers after several weeks of incubation are so little that these bacteria cannot be very important for soil nitrification. Nelson (*Centrl. Bakt.*, 1931, II, **83**, 280) comes to a similar conclusion. Regarding the work of Fremlin, Boltjes states that Fremlin was very likely the victim of an error in technique.

The other approach to the problem has been made by a school of investigators who believe that the organisms of Winogradsky may not be so sensitive to organic substances in the soil as they are in liquid cultures. Wimmer (*Z. Hyg.*, 1904, **48**, 135) made tests with cultures in sand and concluded that organic matter is not so toxic as in solution, but was nevertheless toxic in great concentration. Bazarewski (*Koch's Jahrb.*, 1906, **17**, 452) from similar experiments arrived at the conclusion that 1% dextrose stimulated nitrification, while larger amounts delayed the process

but did not entirely prevent it. Coleman (*Centrl. Bakt.*, 1908, III, **20**, 401) came to a similar conclusion working with sand and the soil cultures. While work with pure cultures may be of great importance when studying the various characteristics of the organisms, it must be conceded that results obtained in such studies cannot be applied *in toto* to the nitrification process in the soil. The soil is a very complex system, being the habitat of numerous heterotrophic and autotrophic organisms. The interplay of these organisms must be taken into account. Many years ago Omeliansky (*Centrl. Bakt.*, 1899, II, **5**, 473) showed that in combination with *Bacterium ramosus*, the nitrite forming organisms can grow and oxidise ammonia even in dilute peptone broth (1 in 20); Boltjes (*loc. cit.*) showed that nitrification can proceed in the usual medium containing in addition peptone and urea, if the medium is inoculated with *Bacterium pseudomonas* and "*urobacillus.*" Pandalai (*Science*, 1936, **84**, 440) found that glucose did not prove harmful and in some cases proved a stimulant to nitrifying organisms in the presence of various heterotrophic organisms like *Azotobacter*, *Bacterium mycoides*, etc.

Moreover, nobody seems to have worked on the influence of the different organic substances that are more likely to be present in normal soils. It will be conceded that glucose, peptone, cane sugar, etc., which have been investigated, would at no time be present in the soil at such high concentrations as to prove detrimental to the action of the bacteria that are responsible for nitrification. The organic matter of the soil results mostly from plant residues, green manure and stable manures. The most important substances added to the soil may be classified into (1) the starches and sugars, (2) pentosans, pectins and other hemicelluloses, (3) true celluloses, (4) lignins and tannins, (5) fats, waxes and fatty acids, (6) proteins and the degradation products of all these substances and lastly (7) the soil humus. A systematic investigation of the influence of these substances at concentrations that are likely to obtain in the soil is necessary. In this paper are reported the results of the study of the influence of humic acid, cellulose, glucose, cane sugar, starch and an amino-acid alanin and the sodium salt of organic acids like citric, oxalic and acetic acids.

EXPERIMENTAL.

The method employed is the liquid culture technique described in Parts I and II of this series.

Influence of Humic Acid.

This is the name given to the final degradation product of organic materials in the soil, a dark coloured material relatively very stable, soluble

in alkalis and precipitated from such solutions on neutralisation with acid. In the following table are reported the results on the influence of humic acid isolated from a garden soil. Merck's humic acid gave similar results.

TABLE I.

Mg. of nitrite nitrogen per litre.

Incubated for	Control.	0·05%.	0·1%.	0·5%.	1%.
5 days	2·2	Nil	Nil	Nil	Nil
15	3·0	6·1	,,	,,	,,
27	18·1	38·1	7·1	,,	,,
37	50·7	74·3	35·4	4·3	5·4
50	124·4	154·5	96.6	41·5	41·8
60	—	185·0	154·5	112·6	98·1

Duplicates were kept in every case.

TABLE II.

Influence of cellulose.

Pure cellulose obtained from cotton fibre by the usual method was used.

3 days	2·5	2·3	2·3		2·2
19	4·2	5·6	8·6		—
26	20·0	31.1	43·1		7·7
34	28·0	45·9	47·7		22·4
45	80·0	124·4	124·4		81·8
57	101·9	131·8	133·3		97·4

TABLE III.

Influence of starch.

3 days	2·5	4·7	4·6	4·0	4·7
19	4·2	Nil	2·1	Nil	Nil
26	20·0	13·0	33·9	,,	,,
34	28·0	22·4	43·9	,,	,,
45	80·0	70·0	124·4	8·0	4·5
57	101·9	115·4	134·4	26·7	22·4

TABLE IV.

Influence of cane sugar.

Merck's pure cane sugar was used.

Incubated for	Control	\Mg. of nitrite nitrogen per litre			
		0·05%.	0·1%.	0·5%.	1%.
3 days	2·5	4·2	4·1	4·4	8·2
9	2·8	Nil	Nil	Nil	Nil
19	4·2	4·0	,,	,,	,,
2ᶠ	20·0	65·9	,,	,,	,,
34	28	82·6	2·9	,,	,,
45	80	140·0	29·5	,,	,,
57	101·9	142·7	56·0	,,	,,

TABLE V.

Influence of glucose.

Merck's pure dextrose was used.

3 days	2·4	1·30	4·5	Nil	Nil
9	7·7	Nil	Nil	,,	,,
19	3·8	,,	,,	,,	,,
26	20·0	16·4	14·0	,,	,,
45	78·3	31·1	78·3	,,	,,
57	112·0	44·8	104·3	,,	,,

TABLE VI.

Influence of organic acids

The sodium salt of the acid was used.

(a) Acetate.

Incubated for	Control	Mg of nitrite nitrogen per litre.		
		0·005 M	0·05 M.	0·2 M.
0 days	2·3	2·3	2·3	2·3
13	3·7	5·6	Nil	Nil
21	5·9	35·6	,,	,,
28	20·7	43·2	,,	,,

TABLE VII.

.(b) Oxalate.

Mg. of nitrite nitrogen per litre.

Incubated for	Control.	o·oo5 M.	o·o5 M.	o·o2 M.
o days	2·3	3·2	3.4	3·8
13	3·7	20·9	4·9	4.0
21	5·9	32·3	3·0	3·7
28	20·7	63·6	4·9	4·7

TABLE VIII.

(c) Citrate.

o	2 3	2·3	2·2	2.3
13	3·7	Nil	Nil	Nil
21	5·9	,,	,,	,,
28	20·7	9·3	6 o	,,

DISCUSSION.

It will be seen from the foregoing tables that humic acid does not inhibit the action of nitrifying bacteria at concentrations in which it is likely to be present in the soil and may even exert a stimulating action on the bacteria. So is the case with cellulose; this substance does not inhibit even at a concentration of 1%. With starch up to o·1 % there is no retardation higher concentrations, o·5 and 1%, however, have a pronounced inhibitory action. Cane sugar up to a concentration of o·o5% does not retard and may even act as a stimulant; higher concentrations will, however. completely stop the growth and respiration of the bacteria ; o·5 and 1% glucose, even at a concentration of o·o5% markedly inhibits the reaction, which is completely brought to a standstill at o·5%. Acetate and oxalate at o·oo5 molar concentration have a beneficial action, while at o·o5 molar concentration they retard the reaction.

It would thus appear that insoluble organic matter like cellulose does not retard the reaction. It is unlikely that the soil contains appreciable amounts of soluble organic matter. Moreover, traces of soluble organic matter like cane sugar, acetate and oxalates may even act as stimulants Humic acid, which is the end-product of the decomposition of different types of organic compounds in the soil and is relatively stable to further decomposition by bacteria and chemical agencies, has a beneficial action on the nitrifying bacteria in concentration in which it is present in most soils. Thus the contention of some workers that soil nitrification cannot be due to the autotrophic bacteria isolated by Winogradsky is untenable.

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Even when the soluble organic matter is present in such high concentrations as to retard the action of the autotrophic bacteria in pure solution culture, we have to take into account the presence in the soil of numerous species of bacteria capable of decomposing organic matter which by their presence create favourable conditions for the action of the autotrophic bacteria. For the reason that organic matter is deleterious to the autotrophic nutrifying organisms in pure solution culture, we cannot rush to the conclusion that these organisms are of little significance for nitrification in the soil; if that be so, we have to assume a soil atmosphere free from oxygen for explaining the existence of anaerobic bacteria in the soil; and it can never be so. The fact is that the aerobic organisms present in the soil create conditions favourable for the growth of the anaerobes by an active utilisation of the oxygen. This can be imitated artificially in the laboratory; when anaerobes are grown readily under ordinary aerobic conditions in the presence of rapidly growing aerobic bacteria like *Bacterium subtilis;* although in the absence of the aerobic organisms, the anaerobes can be grown in pure culture only in the absence of oxygen. Another illustration of the phenomenon is the growth of the two nitrogen fixing organisms, the anaerobic *Clostridium pastorianum* and the aerobic *Azotobacter.* The soil harbours many types of organisms and in order to understand the complete picture of various soil processes in the soil, a knowledge of the mutual interrelations of the different organisms is very essential. Some micro-organims may produce a change in the reaction of the medium or in the oxygen tension, or in the concentration of nutrients or such other factors which may be favourable or otherwise for the growth and chemical activity of other micro-organisms. We have already referred to the fact that in the presence of heterotrophic bacteria like *Azotobacter* and B. *mycoides,* nitrifying autotrophic bacteria can oxidise ammonia even in the presence of glucose.

It will, therefore, be unnecessary to assume as has been done by Russell (*loc. cit.*) and others that nitrification in the soil cannot be due to the autotrophic organisms of Winogradsky but must be due to heterotrophic organisms which tolerate organic matter. As a matter of fact the heterotrophic organisms so far reported to be capable of nitrifying produce only very minute traces of nitrites compared with the very large amounts produced by the Winogradsky organisms. The authors believe that considerable advance in biochemical knowledge can be made by investigations on the mutual interrelations of bacteria.

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THE CYANINE DYES OF THE PYRIDINE SERIES.

By M. Q. Doja.

p-Dimethylaminobenzaldehyde and p-nitrosodimethylaniline have been condensed with the methochloride, methobromide, and methoiodide of 2-methylpyridine, and the properties of the products examined including their absorption spectra and fluorescence.

The cyanine dyes (for a general survey see 'The Cyanine Dyes' by M. Q. Doja, *Chem. Rev.*, 1932, **11**, 273) contain in their molecules the characteristic arrangement, one equivalent of an acid radicle and two nitrogen atoms of basic function joined together by a chain of conjugated double bonds.

(I)

In view of the great sensitising power of (I, X = I), synthesised by Mills and Pope (*J. Chem. Soc.*, 1922, **121**, 946), it was thought of interest to investigate the influence of change of anions on the properties of the compound, and it was with this object in view that the present work was undertaken.

In the first place, the three halides (chloride, bromide and iodide) were chosen for comparison. The chloride corresponding to (I) has been obtained by the condensation of α-picoline methochloride, prepared by a modification of the method of Ramsay (*Phil. Mag.*, 1917, 2, v, 277) with p-dimethylaminobenzaldehyde in presence of piperidine and the corresponding bromide from α-picoline methobromide. These new dyes resemble each other closely and exhibit the general characteristic of cyanine dyes In concentrated aqueous solution all the three substances give rise to orange coloured solutions and brownish yellow solutions in dilute condition. The reddish tinge of concentrated solutions is most predominant in the chloride and least so in the iodide. They dye cotton an orange colour

with a reddish tinge, the variation being the same as in their aqueous solutions. On exposure to sunlight, the dyed cloth begins to fade after three days. All the three compounds give similar absorption spectra showing a band of selective absorption in the blue with a maximum at about λ 4800.

The so-called p-dimethylaminoanils of heterocyclic ammonium compounds (Smith, *J. Chem. Soc.*, 1923, **123**, 2288 ; Bloch and Hamer, *Phot. J.*, 1930, **70**, 374) are desensitisers for the photographic plate (Hamer, *Phot. J.*, 1929, **69**, 409) in contrast to the styryl compounds which are sensitisers.

p-Dimethylaminoanil of 2-methyipyridine methoiodide was first prepared by Kaufmann and Valette (*Ber.*, 1912, **45**, 1736) ; the related chloride and bromide have now been obtained. They are highly coloured like the styryl compounds, and their colour in solution is discharged by mineral acids and restored by alkalis. The three compounds have similar absorption spectra, showing a band of selective absorption in the green with maxima at about λ 5100.

The fluorescence of all the six compounds is shown in Table I.

EXPERIMENTAL.

Absorption spectra were taken in the visible region only with dilute solutions of the compounds in absolute methyl alcohol. The solutions of the styryl compounds were 2×10^{-5} M and those of the anil compounds were 1×10^{-5} M.

The fluorescene was observed with solutions of same strength as employed for taking the absorption spectra, with the help of a thousand candle power point-o-lite lamp as a light source, a lens and condenser and Wallace colour filters Dyeing was performed with tannic acid mordanted cloth.

2-p-*Dimethylaminostyrylpyridine Methochloride.*—A mixture of 2-methylpyridine methochloride (2.5 g., dry) and p-dimethylaminobenzaldehyde (3 g.) in absolute methyl alcohol (45 c.c.) and piperidine (20 drops) was boiled for 9 hours on a sand-bath. After cooling the dark red liquid was left in a vacuum desiccator for 48 hours. The sticky solid, thus obtained, was placed on a porous plate and left in a desiccator for a week. On recrystallisation from methyl alcohol it was obtained as deep red crystals, m.p. 117°, yield 1.8 g. (Found: Cl, 12.6. $C_{16}H_{19}N_2Cl$ requires Cl, 12.9 per cent).

TABLE I.

Colour of the fluorescent beam.

Wallace colour filter No.	Styryl chloride.	Styryl bromide.	Styryl iodide.	Anil chloride.	Anil bromide.	Anil iodide.
1	Very weak red	Weak red	Weak red	Nil	Nil	Nil
2	Very weak red	Red	Red	Weak red	Weak red	Nil
3	Light greenish yellow	Weak orange red	Orange	Pink	Weak red	Very weak pink
4	Very faint pink	Weak orange red	Yellowish red	Yellowish pink	Orange red	Nil
5	Dull yellow	Greenish yellow	Greenish yellow	Greenish yellow	Greenish yellow	Very weak greenish yellow
6	Dull yellow	Greenish yellow	Greenish yellow	Greenish yellow	Greenish yellow	Very weak greenish yellow
7	Dull yellow with an orange tinge.	Green	Dull yellow	Greenish yellow	Green	Nil
8	Dull yellow with an orange tinge.	Weak green	Dull yellow	Bluish green	Bluish green	Nil
9	Yellow	Weak yellow (towards the light, but no trace on the side away from source.	Brownish yellow (appearing towards the source and disappearing towards the side away from the source).	Very weak green.	Nil	Nil
10	Yellow (the end away from the source becoming weaker).	Yellow	Yellow	Yellowish green	Yellowish green	Very weak yellow

Similarly 2-*p-Dimethylaminostyrylpyridine Methobromide* was prepared from 2-methylpyridine methobromide (2 g.) and *p*-dimethylaminobenzaldehyde (2 g.) in absolute methyl alcohol (40 c.c.) with piperidine (0·4 c.c.) by heating for 6 hours. The red liquid was placed in a desiccator for 3 days and the separated solids recrystallised from methyl alcohol in vermillion red silky needles, m.p. 262°, yield 1·6 g. (Found : Br, 24·9. $C_{16}H_{19}N_2Br$ requires Br, 25·1 per cent).

p-*Dimethylaminoanil of 2-methylpyridine methochloride* was prepared from 2-methylpyridine methochloride (2·5 g.) and *p*-nitrosodimethylaniline (2·5 g.) in absolute alcohol (25 c.c.), with piperidine (20 drops) by heating for 9 hours. The crystalline precipitate was recrystallised from methyl alcohol, giving brownish black lustrous needles, m.p. 235°, yield 0·8 g. (Found : Cl, 13·2. $C_{15}H_{18}N_3Cl$ requires Cl, 12·9 per cent).

p-*Dimethylaminoanil* of 2-*methylpyridine methobromide* was prepared from 2-methylpyridine methobromide (1·9 g.) and *p*-nitrosodimethylaniline (1·5 g.) in alcoholic solution with piperidine by heating for 8 hours. The solution was kept in a desiccator and the separated solids recrystallised from methyl alcohol in shining blue black needles, m.p. 237°, yield 0·6 g. (Found : Br, 25·3. $C_{15}H_{18}N_3 Br$ requires Br, 25·0 per cent).

DISTRIBUTION OF TRACE ELEMENTS IN BIOLOGICAL MATERIAL.

By A. L. Sundara Rao.

In continuation of previous work, representative types of cereals, pulses and leafy vegetables have been analysed and the results reported in this paper. Methods devised for the spectrographic analysis of mineral substances have been applied for the identification and estimation of trace elements. Many interesting results have been obtained in this way. It is pointed out that the methods should be specially useful to those interested in problems of animal and human nutrition.

The wide distribution of elements in minute quantities in biological materials has been regarded until lately as accidental. In recent years, a number of papers have been published on the presence of trace elements such as Mn, Ti, B, Zn in soil and the marked influence they exert on the microbial population and on plant growth. The importance of traces of manganese for the plant has been demonstrated by McHargue, McLean, Kelley and Gerrestsen (*Trans. Third Int. Cong. Soil Sci.*, 1935, **1**, 189). The occurrence of molybdenum and vanadium in nature has been well studied by Meulen (*Rec. trav. chim.*, 1932, **51**, 549), Dingwell (*Candian J. Res.*, 1934, **11**, 32), Horner (*J. Agric. Res.*, 1934, **48**, 981) and others. Hoagland (*Trans. Int. Cong Soil Sci.*, 1935, **3** 216) found that zinc salts have a striking curative effect in diseases of fruit trees, known as "mottled leaf". Author's own experiments (*Proc. Indian Acad. Sci.*, 1937 **6B**, 91) have shown that soil fertility is in a measure due to the predominating proportion of manganese and zinc.

Hart and co-workers have shown (*J. Biol. Chem.*, 1928, **77**, 797) the importance of copper as a supplement to iron for haemoglobin regeneration in the rat. Manganese was found by Wilgaus, Norris and Heuser (*J. Nutrition*, 1937, **14**, 155) and Caskey and others (*ibid.*, 1939; **17**, 407) to be markedly effective in preventing the incidence of "perosis" in chicks. The rôle of zinc in the nutrition of rats and pre-school age children has been investigated by Stirn and others (*J. Biol., Chem.*, 1935, **109**, 347) and Scouler (*J. Nutrition*, 1939, **17**, 103). The deleterious effects of molybdenum on milking casttle has been pointed out by Lewis and co-workers (*Nature*, 1938, **141**, 553).

Very little work has been done in India on the rôle of these micro-constituents in animal and human nutrition and no attempts have been made to estimate quantitatively the amounts of such elements as Mn, Zn, Mo in some of the widely consumed Indian foodstuffs. The only references

in the literature in this direction are those of Boyd and Dey (*Indian J. Med. Res.*, 1933, **21**, 109), Rudra (*J. Indian Chem. Soc.*, 1939, **16**, 132) and Newcomb and Sankaran (*Indian J. Med. Res.*, 1929, **16**, 788) regarding the quantitative estimation of manganese. Before any work could be undertaken on the nutritive value of a particular foodstuff, complete data regarding the distribution of major and the minor constituents of the foods will be invaluable.

For the detection and estimation of the minor constituents micro-chemical methods have been and are being widely used. The superiority of spectographic methods has been previously pointed out by the author (*loc. cit.*).

In continuation of the previous work (*Science & Culture*, 1938, **4**, 362) further representative types of cereals, pulses and leafy vegetables have been analysed and the results are reported in this paper.

EXPERIMENTAL.

In preparing the samples for analysis they were carefully washed with distilled water, spread out in thin layers and left until the water had evaporated. They were then cut into small pieces, dried to a constant weight at 100°, ground in a glass mortar and bottled. The samples were ignited over a Bunsen flame in a platinum crucible at a temperature less than 450°. This method of ashing gave entirely satisfactory results and the use of a muffle seemed quite unnecessary Provided that the flame is not allowed to play directly on the specimen, there is no reason to suppose the possibility of contamination with the material of the burner.

For photographing the spectra, a Hilger medium quartz spectrograph was used. The plates used for the ultraviolet and near ultraviolet were "Imperial Special Rapid," while for the visible region "Eastman Panchromatic" plates, which have a considerable and fairly uniform sensitivity from 6,700 to 4,000Å were used.

The arc spectra of the elements contained in the above specimens were excited using silver and graphite electrodes. Owing to the low temperature of the silver arc some elements like Mn, Ni, Co, and B might escape detection. Further it was felt that for other elements good corroboration could be obtained by comparing results in both types of arc. The electrodes were supplied by Adam Hilger and reported to be H. S. brand purity and accompanied by full chemical and spectroscopic reports on their composition. The electrodes were prepared so that the positive rod contained a cavity 2 mm. wide and 4 mm. deep into which weighed amounts of the sample were introduced. The negative was sharpened to a fine

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point. This pointed electrode aided in centering and confining the arc, thereby reducing its tendency to wander. The variation of the arc current was never more than ±0·05 ampere.

The essential feature of the method used in the course of this work for the determination of the concentration is a comparison of the line intensities. Spectrograms were obtained from prepared samples made up in concentrations from 1 part in 100 down to the limit of sensitivity. The particular line chosen for the determination of the element was microphotographed in all the spectra and a curve was constructed showing the relation between the percentage of the element and the intensity produced on the photographic plate. From the known intensity of the line in the test spectrum, the percentage composition of the element could be determined by interpolation from the curve.

While this paper contents itself with a qualitative identification of the major elements, a quantitative estimation is done for Mn, Zn, and Mo. For the detection and estimation of Zn, the line 2138.6Å, the most sensitive of zinc lines was used, while for Mo the three lines 3798, 3864, and 3903 Å which form the "raies ultimes" were used. For Mn, the triplet 4034·45, 4033·07, 4030·76 Å was adopted.

Four different samples of each were analysed and the average results of estimations are given in Table I. Typical spectrograms are shown in Plates I and II.

TABLE I.

English name	Bot. name.	Moisture.	Ash.	Mn	Zn	Mo	Remarks.
				expressed per kg. of dry materials.			
Rice (polished)	Oryza sativa	12·4%	1·19%	12 6 mg	2·0 mg	0·1 to 0·72 mg	There was a wide variation from sample to sample, so only the limits are given and it can be said that cereals vary within these limits as regards their Mo content
Wheat (whole grain)	Triticum vulgare	12·8	1·30	36·4	20·4		
Bengal gram	Circer arieti-num	9·8	3·03	28·6	19·4	2 0	
Black gram	Phaseolus mungo	10·9	3·70	24·0	26·5	4·5	
Peas (green)	Pisum sativum	78·6	4·10	18·1	40·2	9·4	
Amaranth (tender)	Amarnathus gangeticus	86·1	23·1	60·2	26·8	<1	
Spinach	Spinacea oleracea	92·3	23·3	82·3	62·3		Purchance present only in very minute traces
Cabbage	Brassica oleracea capitata	92·4	11·2	11·8	23·5		

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DISCUSSION.

From the spectrograms reproduced the variation in the concentration of the different elements is very striking. There is a continuous increase in the proportion of sodium and alkaline earth metals and iron as we go from cereals to pulses and leafy vegetabes.

The leafy vegetables are generally rich in iron though spinach contains comparatively less of this element. It is seen from the results that wheat is comparatively rich in manganese than rice and it is interesting to draw attention to the work of McCarrison (*Indian J. Med. Res.*, 1927, 14, 641) on the effect of Mn in foodstuffs and its bearing on the growth of animals We have an analogy of the favourable effects of manganese on plant growth and the results reported here also support the observations of McCarrison, and suggest that it plays a definite rôle in human nutrition as well. Molybdenum is found in fairly large amounts in all pulses, peas and black gram containing the largest amounts. Next in order are the cereals, and the leafy vegetables contain the least amounts of Mo which is present only in very minute traces. Nickel is present in small but detectable quantities. The evidence for Co and vanadium is not definite. The observations of Boyd and De (*Indian J. Med. Res.*, 1933, 20, 789) regarding the presence of vanadium in rice and wheat could not be verified. The cereals are relatively rich in Rb and Sr. The most remarkable feature is the extraordinarily high magnesium content of spinach.

It would seem from the results that the so called trace elements are really present in appreciable amounts and would possibly play a definite and specific rôle in animal and human nutrition. The assessment of the nutritive value of a particular foodstuff would be incomplete without a proper understanding of the exact rôle of these minor constituents.

Explanation of Plates.

The spectograms reproduced here are enlargements of certain regions of the spectra of representative specimens of cereals, pulses and leafy vegetables with the blank spectra of electrodes.

Plate I: Fig. 1. shows the Sr line 4608 intensified in wheat.
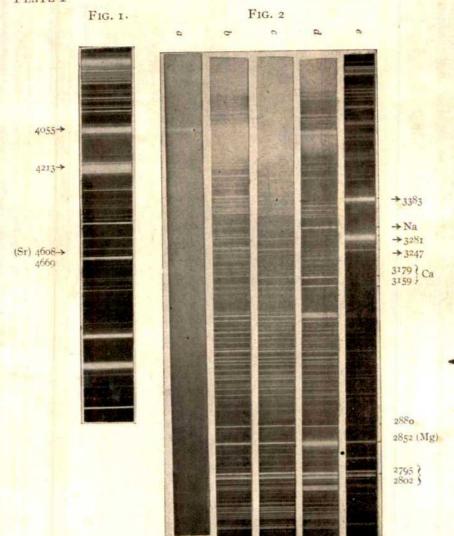
In each of the other figures, (a) is the spectrum of the blank electrodes, b, c, d are the spectra of rice, black gram and spinach respectively; e is the spectrum of Ag arc comparison.

Plate II, Figure 4 shows comparison standards for estimating zinc.

PLATE I

FIG. 1.

FIG. 2

a   *b*   *c*   *d*   *e*

4055→

4213→

→3383

→Na
→3281
→3247

3179 } Ca
3159 }

(Sr) 4608→
4660

2880

2852 (Mg)

2795 }
2802 }

PLATE II

FIG. 3.

3247
3281
3302
3306
3383 →
(K) 3447 →
(Mn) →
4213 →

FIG. 4.

FIG. 4(A)

(Zn) 2138·6 →
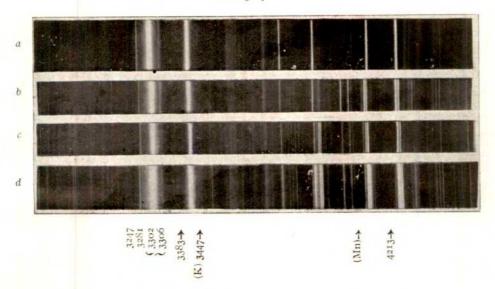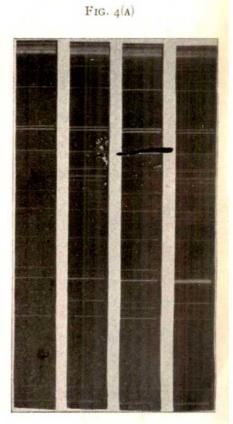
(Zn) 2138·6 →

d   c   b   a

20 mg.   40 mg.   60 mg.   100 mg.

ISOLATION OF ANTI-ANAEMIC FACTOR PRESENT
IN RAW LIVER.

By S. K. MITRA.

That raw liver contains a principle potent against pernicious anaemia had been recognised long ago. That this principle is essentially organic in nature, is rendered very probable by the work of Dakin, Karrer and others (*J. Biol. Chem.*, 1928, **77**, 325 ; 1930, **88**, 428 ; 1935, **109**, 438 ; 1928, **77**, 331 ; 1931, **92**, 117 ; *Am. J. Physiol.*, 1929, **90**, 336 ; *Helv. Chim. Acta*, 1938, **21**, 314 ; 1937, **20**, 622.) The problem of isolation of the active principle was taken up in 1936 in the Biochemical Laboratory of the King's College, London, and has been continued in the University College of Science, Calcutta. It has now been possible to isolate a purely organic substance which has been proved by clinical tests, to possess powerful reticulocytic activity. It is free from all traces of metals and has been proved to be not an amino-acid. It does not give "Pauly reaction", nor does it respond to the "Ninhydrin test." It is not a polypeptide. The substance contains sulphur and nitrogen and forms a picrate, m.p. 235°. (C, 38·34 ; H, 2·89 ; N, 19·38 per cent).

The material was further fractionated by liberating it from the picrate at different p_H values in the acid range. The compound isolated at p_H 0·5 is highly active and forms a picrate in yellow cubes, m.p. 245°. (Found : N, 20·7 per cent).

The depicrated material is a colourless body, precipitable by phospho-tungstic acid and gives pyrrole reaction. By clinical test it has been found to be potent against anaemia either when injected or administered orally. A detailed account of the results will be soon published.

Sulphur forms a part of the constitution of the active material since it gives a crystalline compound with mercuric chloride.

A NOTE ON THE LECITHIN CONTENT OF THE BLOOD OF INDIAN WOMEN IN NORMAL CONDITION AND IN PREGNANCY.

By HEMENDRA NATH CHATTERJEE AND SURATH MOHAN GHOSH.

The lecithin content of the whole blood has been determined by the method of Whitehorn (*J. Biol. Chem.*, 1924, **62**, 133). The blood was examined in 25 normal non-pregnant women and 25 women in the different terms of pregnancy from fifth month upto nearly the term. The figures in the following table show that there is a distinct rise in the figures for lecithin during pregnancy.

Normal pregnancy.		Normal females.	
Case No.	Amount in mg. per 100 c.c. of blood.	Case No.	Amount in mg per 100 c.c. of bloo
1	13·3	1	9·5
2	12·5	2	9·5
3	13·3	3	9·1
4	11·1	4	10·0
5	10·5	5	6·8 (Lowest)
6	11·1	6	7·4
7	12·5	7	8·7
8	11·1	8	10·0
9	12·5	9	8·7
10	12·5	10	11·1 (Highest).
11	16·6	11	11·1
12	13·3	12	11·1
13	11·1	13	9·5
14	11·2	14	8·7
15	13·3	15	9·5
16	14·2	16	9·5
17	12·5	17	9·5
18	16·2	18	10·0
19	17·0 (Highest)	19	8·3
20	13·3	20	11·1
21	11·5	21	9·0
22	12·5	22	9·5
23	10·5	23	10·0
24	10·0 (Lowest)	24	9·1
25	10·3	25	7·0
Average	12·54	Average	9·34
Standard deviation	±1·87	Standard deviation	±1·14

The blood was drawn between 10 and 12 A.M. and on empty stomach.

Our thanks are due to Prof. C. C. Basu for his help and advice.

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A NOTE ON SOME OF THE ELECTROLYTES OF THE SERUM IN NORMAL INDIANS

By Hemendra Nath Chatterjee and S. Sen.

The following electrolytes have been estimated, *viz.*, sodium, potassium, magnesium and calcium in the blood serum of apparently normal Indians.

The subjects used for observation were adults, of ages varying from 14 to 45 and belonging to both the sexes. The blood was taken on empty stomach between 11-30 a.m. to 12-30 p.m. from the median cubital vein. It will be observed that the figures for calcium are slightly lower and that for magnesium somewhat higher than the figures given by Peters and Van Slyke ("Quantitative Clinical Chemistry," 1932, p. 753) and also by Cameron ("Text Book of Biochemistry", 1933). No appreciable variations were observed due to the difference of sex.

Table I showes the concentrations of sodium, potassium, magnesium and calcium in mg. per 100 c.c. of blood serum.

TABLE I.

Total No. of cases.				
	30	15	30	30
Male	21	6	23	20
Female	9	9	7	
	Sodium.	Potassium.	Magnesium.	Calcium.
Highest	378·0	26·0	4·5	12·6
Lowest	289·0	15·0	2·3	7·4
Average	325·0	20·4	3·3	9·5
Mean deviation	±28·0	±3·5	±0·7	±1·6
Average figure of Hald, Peters and van Slyke (19 cases).	308·0	18·3	2·0	10·0
Average of Cameron per 100 g. of plasma.	150-250	16-22	2·3	10-11
Average figures obtained by other workers.	Rourke (14 cases) 339 mg. per 100 c.c. serum.	Kramer and Tisdall (10 cases) 19 6 mg. per 100 c.c. serum.		Kramer and Tisdall 9·2—10·3 ; Mukherjee (19 cases) 9·6 per 100 c.c. serum.

The respective methods that have been used by us are given below:

For sodium we have adopted the method of Dorothy Rourke (*J. Biol. Chem.*, 1928, **78**, 337); for potassium that of Kramer and Tisdall (*J. Biol. Chem.*, 1921, **46**, 339); for magnesium that of Haury's (*J. Lab. Clin. Med*, 1938, **23**, 1079) modification of the method of Hirschfelder and Serles (*J. Biol. Chem.*, 1934, **104**, 635); for calcium that of Kramer and Tisdall (*J. Biol. Chem.*, 1921, **47**, 75).

A RAPID METHOD OF ESTIMATING TUNGSTEN IN TUNGSTEN STEELS.

By Durga Pada Chatterjee.

For the quick estimation of tungsten in tungsten-steels (high speed steels or self-hardening steels as they are called) a method has been evolved in which tungsten is oxidised to tungstic acid, dissolved in excess of caustic alkali, the excess of which is back titrated by a standard acid, glycerol and mannitol being used to prevent hydrolysis.

Steel-borings (2g.) are dissolved in 60 c.c. of concentrated HCl. When the solution is almost complete HNO_3 is added drop by drop for oxidation and the solution evaporated with occasional addition of drops of nitric acid. Yellow precipitate of WO_3 comes out. The concentrated solution is then diluted with 100 c.c. of 10% HCl solution when heavy precipitation occurs. This is filtered through paper pulp (Swedish paper pulp being preferable), and washed with 1% NaCl solution till free from acid. It is then mixed with 50 c.c. of warm water with 40 c.c. of neutral glycerol or 1.5 g. of mannitol and vigorously shaken. $N/10$-NaOH solution is then added with constant stirring till the yellow precipitate goes into solution and the liquid becomes colourless. The excess of NaOH is then titrated by $N/10$-HCl

This method has been found to be applicable to steels containing as much as 4 to 20% of tungsten.

The author's thanks are due to Mr. C. H. Shvitcliff, the Head of the Laboratory for his encouragement and interest.

ADSORPTIVE PROPERTIES OF SYNTHETIC RESINS.
PART IV.

BY S. S. BHATNAGAR, A. N. KAPUR AND M.S. BHATNAGAR.

The adsorption of homologous series of mono- and dibasic aliphatic acids by acid- and alkali- condensed phenolic resins, amino- and protein resins has been studied. The reversal of Traube's rule in the case of alkali-condensed, amino- and protein resins is explained on the basis of orientation of molecules at the resin-solvent surface according to the theory put forward by Langmuir and Harkins. The influence of various substituents on adsorption has also been studied. The adsorption by ammonia-condensed amino- and protein resins increases with the introduction of COOH, OH, CN, Cl, Br. The NH₂ and alkyl groups cause a decrease in adsorption.

The results obtained in the case of acid phenolic resins are quite the opposite to those in basic resins. This is probably due to the fact that acid resin is less polar than water. In non-polar solvents results are in line with those obtained in basic resins.

Bhatnagar, Kapur and Puri (*J. Indian Chem. Soc.*, 1936, **18**, 679) have shown that the order of adsorption of organic acids in a homologous series by acid-condensed phenolic resins follows Traube's rule. S. Tsuruta (*J. Soc. Chem. Ind. Japan*, 1938, **41**, 129B) found that the order of the series was reversed when ammonia-condensed resins were used as adsorbents. This was also confirmed by observations in this laboratory and an explanation was given in a previous paper (*J. Indian Chem. Soc.*, 1939, **16**, 261) on the basis of the pores of the resin. It was shown that the adsorption of the acids by amino- or ammonia-condensed resins increased as the ionisation constant increased and the reverse holds good for acid-condensed phenolic resin. The present work has been undertaken to throw more light on this subject and to give a possible explanation which may account for all the facts. These reversals are known to occur in the case of gold (Heymann and Boye, *Kolloid Z.*, 1932, **59**, 153) and silica gel (*J. Phys. Chem.*, 1928, **32**, 522). Heymann and Boye (*loc. cit.*) studied the adsorption of acetic, propionic, butyric and caproic acids from water, CCl₄, C₆H₆, alcohol, and acetone by metallic gold and experienced the reversal of Traube's rule. This was explained by the fact that the highly polar group—COOH in solution oriented towards polar gold particles and the non-polar alkyl part towards the solvent. Since with the increase of the hydrocarbon chain the molecule becomes less polar, the higher fatty acids are therefore less adsorbed by gold. The adsorption of various aliphatic acids has been studied and attempts have been made to

explain the amounts adsorbed on considerations based on polarity of the resin, the solvent, and the adsorbate.

EXPERIMENTAL.

Preparation of the Resins.

Amino- and Phenolic Resins.—Amino- and phenolic resins were prepared as described in the previous paper (*loc. cit.*).

Protein Resins.—The powdered soyabean meal was stirred into a 10% solution of sodium chloride at 40° and filtered through glass wool. The protein was precipitated from the milky suspension by the addition of dilute acetic acid. A colourless precipitate was obtained on standing. This was filtered, washed with methyl alcohol till free from chloride ions, acetic acid and starch.

10 G. of dried protein thus prepared, were refluxed with 60 c.c. of formalin (40% formaldehyde) for 2 to 3 hours. It was then filtered, washed with hot water until free from formaldehyde. The resin was dried and sieved through 100 mesh.

Adsorption Experiments.—The adsorption experiments were carried out in stoppered glass bottles which were thoroughly cleaned, steamed and dried. The powdered resin (1 g.) was weighed out in each bottle and 100 c.c. of the aqueous solutions of the acids were run in. The bottles were vigorously shaken for 5 minutes and set aside for 36 hours to attain equilibrium. The supernatant solution (10 c.c.) was pipetted out and run into excess of standard sodium hydroxide solution. The equilibrium concentration (C_e in millimoles per litre) was determined by titrating the excess of caustic soda against standard hydrochloric acid. Blank experiments were run side by side which gave the original concentration (C_0 in millimoles per litre). The difference ($C_0 - C_e$) gave the amount adsorbed (X, in millimoles per g. of the resin) from 100 c.c. of the aqueous solutions.

TABLE I.

%Sorption of monocarboxylic acids by 1 g. of resin from 100 c.c. of their 0·01 M aqueous solution.

Acids.	Resorcinol-formalin resins.		m-Phenylenediamine-formaldehyde resin.	Protein-formaldehyde resin.
	HCl condensed	NH₃ condensed.		
Formic	3·32%	20·04%	33·65%	3·32%
Acetic	5·50	13·00	31·5	1·00
Butyric	8·11	12·18	22·84	0·00

TABLE II.

% Sorption of acids by 1 g. of resin from 100 c.c.
of their solution in benzene.

Acids	Resorcinol-formalin resins.		m-Phenylene diamine- formaldehyde resins.	Protein resins
	HCl-condensed.	NH$_3$-condensed.		
Formic	33·7%	63·8%	87·4%	30·0%
Acetic	20·7	40·0	54·6	19·0
Butyric	18·0	35·2	48·6	16·0

TABLE III.

% Sorption of acids by 1 g. of resin from 100 c.c.
of their solution in carbon tetrachloride.

Formic	52·8%	84·5%	97·7%	42·6%
Acetic	40·7	65·5	73·8	30·7
Butyric	32·1	52·08	61·5	26·0

TABLE IV.

% Sorption of acids by 1 g. of resin from 100 c.c.
of their solution in chloroform.

Formic	13·8%	31·0 %	78·1%	10 0%
Acetic	10·7	25·8	46·2	8·6
Butyric	9 5	11·5	18·4	4·5

TABLE V

% Sorption of acids by 1 g. of resorcinol-formaldehyde resin
(acid-condensed) from various solvents.

Solvents.	Dipole moments* of the acids	Water	CHCl$_3$.	C$_6$H$_6$.	CCl$_4$
*Dipole moments of the solvents × 10 [10]	$\rightarrow$	1·85	0·95	0·2	0
Formic	1·45%	3·3%	13·8%	33·0%	52·8%
Acetic	1·04	5·5	10·7	20·7	40·7
Butyric	0·93	8·1	9·5	18·0	32·1

* The values for dipole moments have been taken from *Z. physikal. Chem.*, 1930, B10, 220

An examination of Tables I to V shows that

(1) In aqueous solutions the adsorption of a homologous series of fatty acids on acid phenolic resins follows the normal order. But in basic phenolic resins and amino-resins the order is reversed (Table I).

(2) In non-polar solvents the Traube's rule is reversed even in the case of acid phenolic resins (Tables II, III and IV).

(3) As the dipole moment of the solvent decreases the percentage sorption increases, the sorption being maximum in the case of carbon tetrachloride which has a zero moment.

All the above facts can be easily explained on the Langmuir-Harkins theory of surface orientation if we assume that the acid phenolic resins are less polar than water and the basic phenolic resins and the amino-resins are more polar than water. In support of this we have the observation of of Megson and Drummond (*J. Soc. Chem. Ind.*, 1930, **49**, 251T) who found that when phenol and formaldehyde are condensed in presence of an acid 2 : 4-di-hydroxyphenylmethane

$$\left(\underset{OH}{\bigcirc}-CH_2-\underset{OH}{\bigcirc} \right)$$

is formed. While using an alkaline catalyst hydroxybenzol alcohols

$$\left(\underset{CH_2OH}{\bigcirc}OH \right)$$

are formed. Pollak and Riesenfeld (*Z. angew. Chem.*, 1930, **43**, 1129) have found that by the basic condensation of phenol and formaldehyde, the benzol alchohols formed gives low molecular products which have a strongly polar character.

According to Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221) and Harkins (*ibid.*, 1917, **39**, 354) the surface tension phenomena in general are dependent upon the orientation and packing of the molecules in surface layers and the forces involved in that action are related to those involved in solution and adsorption.

The presence of one of the strongly polar groups such as -OH, -CHO, -COOH, in molecules confers on them the property of solubility in a polar solvent like water. As the length of the hydrocarbon chain increases the solubility of the molecule markedly decreases. The diminution in solubility is probably not due to any weakening of the force of attraction between the water and the polar group. The active groups such -OH, -COOH, -Br, ·Cl strive to penetrate the surface of water and do so provided that the hydrocarbon residue is not too large. If the hydrocarbon chain is too long, the attractive force between the polar group and the polar water, though still the same as before, is not sufficient to pull the long chain into the water. So, the polar group is oriented towards and possibly dissolved in the water, whereas the hydrocarbon chain points away and is out of the

water surface and so dissolution is prevented. Bartell and Millar (*J. Phys. Chem.*, 1924, **28**, 992) also came to similar conclusions from their results on the adsorption of organic acids on carbon.

Now in a basic resin-water interface, the resin is more polar than water and the fatty acid molecules will orient themselves so that the polar -COOH group is oriented towards the more polar resin surface and the non-polar alkyl group is oriented towards water. As we ascend the homologous series, though the force between the polar surface and the end -COOH group remains constant, the long hydrocarbon chain becomes increasingly difficult to pull into the polar surface. The molecule therefore has a tendency to go more into water or at least to assume a tilted position. Thus it will take more of the resin surface in the tilted position than if it were in the vertical position. Hence lesser number of molecules will be adsorbed with increase in molecular weight. This explains the reversal of Traube's rule in alkali-catalysed resins. Further, as is well known in the case of fatty acids, the molecular association decreases with the increase in hydrocarbon chain. So there are greater possibilities for the packing effect due to superimposition of the carboxylic groups in the lower fatty acids than in their less associating higher homologues because in the latter case the molecules will cover more of the resin surface. Therefore, we should expect a decrease in adsorption with increase in molecular weight as has been observed.

In the case of an acid-catalysed phenolic resin, it being less polar than water, the polar -COOH group will tend to orient more towards water. In the case of higher homologues, though the force between water and the polar -COOH group is constant, it is more difficult to pull the longer chain into water and the balance of distribution of the acid between water and the resin shifts towards the resin. So we should expect results opposite to those obtained in the case of basic resins *i.e.*, the adsorption increases with increase of molecular weight.

This view is further supported by the results tabulated in Table VI. In ammonia-condensed and amino-resins the adsorption of the *cis*-form is greater than that of the *trans*-form.

When both the carboxylic groups are oriented towards the resin surface, the substance should be expected to get adsorbed more than when only one is oriented towards it. The adsorption of citraconic acid is greater than that of fumaric acid but less than that of maliec acid due to the decrease of polarity by the introduction of the positive $-CH_3$ group. The order of adsorption is reversed in the case of acid-condensed resin as was to be expected.

TABLE VI.

% Sorption of the acids by 1 g. of the resin from 100 c.c. of $0.01M$-soln.

Acids.	Constitution.	Protein formaldehyde resin.	m-Phenyl-enediamine-formalin resin.	Resorcinol-formaldehyde resin.	
				NH$_3$-cata lysed.	HCl-cata-lysed.
Fumaric	H—C—COOH ‖ COOH—C—H	15·35%	71·43%	26·73%	2·57%
Maliec	H—C—COOH ‖ H—C—COOH	32·33	80·70	43·36	2·00
Citraconic	CH₃ - C—COOH ‖ H—C—COOH	27·00	74·90	36·61	2·20

TABLE VII.

% Sorption of acids by 1 g. of resin from 100 c. c. of their $0.01M$-aq. soln.

Acids	Resorcinol-formaldehyde resin.		m-Phenylene-diamine resin.	Protein resin	Ionisation constant
	HCl cata-lysed.	NH$_3$ cata-lysed.			
Formic	3·3%	20·04%	33 65%	3·3%	$2·14 \times 10^{-4}$
Acetic	5·5	13·00	31·50	1·0	$1·86 \times 10^{-6}$
Butyric	8·1	11·42	22·84	—	$1·48 \times 10^{-5}$
Oxalic	1·75	34·60	74·40	25·00	$3·80 \times 10^{-2}$
Malonic	2·27	24·40	68·30	14·83	$1·61 \times 10^{-3}$
Succinic	2 85	16·30	47·20	3·00	$6·6 \times 10^{-5}$
Aconitic	1·00	26·51	80·00	19·10	$1·33 \times 10^{-3}$

Table VII shows the sorption of mono-, di-, and tricarboxylic acid by acid- and alkali-catalysed phenolic resins, m-phenylenediamine and protein resins. In the previous paper an explanation for the order of adsorption was given on the basis of the ionisation constant of the acid and on the accomodability of the molecule in the capillary structure of the resin. Although this view explained satisfactorily the order of adsorption in a homologous series, but it will be clear from an examination of Table VII that there is no general relation between the ionisation constants and adsorbability when members of different series are taken into account e.g. why oxalic and malonic acids having much greater ionisation constants than formic, acetic and butyric acids should have lesser adsorption in acidic

resins. This discrepancy can be easily explained on the polar concept. The dibasic acids having two polar groups would have greater tendency to get oriented towards the more polar water than towards the comparatively small polar resin surface. It is interesting to note that the adsorption of oxalic and malonic acids in ammonia-catalysed and m-phenylenediamine resins is almost double that of formic and acetic acids respectively This is probably due to the fact that each of the latter acids differs from the former in having one hydrogen replaced by a $-COOH$ group. The addition of another $-COOH$ group would naturally be expected to give an equal increment to adsorption. They will, therefore, have lesser adsorption in acid resins as already explained. Aconitic acid having three polar carboxyl groups is adsorbed least of all.

From Table VIII it is clear that as more polar groups are introduced in the molecule, the adsorption also increases in ammonia-condensed and amino-resins, while it decreases in an acid-condensed resin.

The polarisability due to orientation is given by $\mu^2/3kT$ where μ is the dipole moment, k is the Planck's constant and T, the absolute temperature. In our experiments T and K remain constant. Therefore the greater the

TABLE VIII.

% Sorption of substituted acids by 1 g. of resin from 100 c.c. of their
0·01 M aq. soln.

Acids	Resorcinol-form-aldehyde resin.		m-Phenylene-diamine resin.	Protein resin.	Ionisation constant.	Dipole* moment of groups $\times 10^{18}$.
	Acid condensed.	NH$_3$ condensed.				
Acetic	5·5	13·0	31·50	1·0	$1·85 \times 10^{-5}$	—
Chloroacetic	2·05	30·69	62·50	12·9	$1·52 \times 10^{-3}$	2·0
Dichloroacetic	1·30	40·88	77·46	30·05	$5·00 \times 10^{-2}$	4·0
Trichloroacetic	—	42·15	82·55	33 96	$2·00 \times 10^{-1}$	6·0
Cyanoacetic	1·94	33·50	67·00	14·56	$3·56 \times 10^{-3}$	3·5
Hydroxyacetic (glycollic)	2·30	18·81	35·64	2·40	$1·51 \times 10^{-4}$	1·7
Aminoacetic (glycocoll)	13 5	0·0	2·5	0·0	$3·40 \times 10^{-10}$	1·3
Propionic	5·5	13·0	31·5	1·00	$1·40 \times 10^{-5}$	—
Chloropropionic	9·0	20·39	49·52	6 50	$1·47 \times 10^{-3}$	2·0
Hydroxypropionic (lactic)	13 8	16 00	33·50	2 00	$1·38 \times 10^{-4}$	1·7
Aminopropionic	35·5	9·70	16·10	—	$9·00 \times 10^{-10}$	1·3

* The values for the dipole moments for the groups are taken from " The Dipole moments and Chemical Structure " by Debye.

dipole moment, the greater would be the polarisation. The dipole moment will in its turn depend on the moments of the groups introduced. Hence the greater the moment of the group, the greater will be the polarisability in the substituted acids. In case of ammonia-condensed and amino-resins the percentage adsorption increases with the increase of group moments, which is as should be expected. Thus we see that in the case of substituted acids also the polar view holds good. Since NH_2 group has a moment opposite to that of other groups, the decrease of adsorption in the case of amino-acids is also explained satisfactorily.

TABLE IX.

% Sorption of ketonic acids by 1 g. of the resin from their
100 c.c. of 0·01M-aq. soln.

Acids.	Resorcinol-formaldehyde resin.		m-Phenylene-diamine resin.	Protein resin.
	Acid- condensed.	NH₃- con-densed.		
Pyruvic (acetoformic)	3·14%	32·50%	55·0%	18·0%
Laevulinic (acetopropionic)	10·50	13·80	34 0	—

From Table IX it is clear that the percentage adsorption of ketonic acids also increases with increase of molecular weight in the case of acid-condensed resin, while the reverse holds good in the case of ammonia-condensed and amino-resins.

TABLE X.

% Sorption of substituted succinic acids by 1 g. of resins
from 100 c.c. of their 0·01M aq. soln.

Acids.	Resorcinol-formaldehyde resins.		m-Phenylene-diamine resin.	Protein resin.	Group moment × 10¹⁸.
	Acid-con-densed.	NH₃-con-densed.			
Succinic	2·85%	16·3%	47·20%	8·0%	—
Dibromosuccinic	—	25·0	61·10	23·47	3·8
Malic	2·00	16·66	48·30	8·16	1·7
Tartaric	0·75	18·84	52·0	10·10	3·4
Aminosuccinic	15·61	11·2	14·1	2·44	1·3

Table X shows the effect on adsorption of succinic acid of the introduction of different groups. It will be seen that as in the case of substituted acetic acids, the introduction of halide and hydroxyl groups increases the adsorption in basic resins and decreases it in acidic resins. The amino group having an opposite polarity causes reverse results in both the resins.

From Table XI we find that with the introduction of OH and carboxylic groups the adsorption increases. The adsorption is increased to a greater extent by the COOH group than by the OH group which is as should be according to group moments.

TABLE XI.

% Sorption of hydroxy acids by 1 g. of resin from 100 c.c. of their o·o1M-aqueous solution.

Acids.	Resorcinol-formaldehyde resin.		m-Phenylene-diamine resin.	Protein resin.
	Acid-condensed.	NH$_3$-condensed.		
Lactic	13·8	16·0	33·5	—
Glycollic	2·3	18·81	35·64	2·4
Malic	2·0	16·16	48·3 ·	8·16
Tartaric	0 75	18·84	52·0	10·1
Citric	0·50	18·22	63·05	12·8

From the above results we come to the conclusion that amino-and alkali-condensed resins behave as strongly polar substances while the acid-condensed resins behave as non-polar or weakly polar substances.

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HETEROGENEOUS REACTION BETWEEN CHROMIC SULPHATE AND MANGANESE DIOXIDE.

By Mata Prasad and M. A. Naqvi.

The velocity of the heterogeneous reaction between finely divided powdered manganese dioxide and chromium sulphate solution has been studied. The reaction is concluded to be analogous to the decomposition of ammonia.

Prasad, Naqvi and Shetgiri (*Current Sci.*, 1939, **8**, 361) have shown that when a solution of chromium sulphate is shaken with solid hydrated manganese dioxide, dichromate ions are formed in the solution. According to them the reaction takes place as

$$Cr_2(SO_4)_3 + 3MnO_2 + H_2O = 3MnSO_4 + H_2Cr_2O_7.$$

The correctness of the above equation has been established by them by performing several quantitative experiments.

The present investigation deals with the velocity of the heterogeneous reaction between finely powdered manganese dioxide and a solution of chromium sulphate.

EXPERIMENTAL.

Hydrated manganese dioxide was prepared by the method described by Chatterjee (*Chem. News*, 1921, **123**, 232). A solution of Merck's pure manganese sulphate containing a small quantity of potassium nitrate was gently heated and a solution of potassium permanganate was added to it drop by drop, with constant stirring, until the supernatant liquid was distinctly pink. The precipitated manganese dioxide was washed free from impurities and then dried at about 50°. On analysis the oxide gave moisture, 13·75%; Mn, 54·94%; O_2, 31·31% (Mn : O = 1 : 1·969).

This was passed through sieves of different meshes and various fractions between two sieves were collected and carefully stored.

Solution of chromium sulphate was prepared from Merck's pure substance and its concentration was determined in terms of dichromate formed by oxidising it with sodium peroxide. Solutions of different concentrations were prepared from this stock solution by diluting it suitably.

The sieved dioxide (0·25 g.) was taken in each of the seven conical flasks and 50 c.c. of the chromium sulphate solution were added to each,

The flasks were then shaken on a shaking machine placed in the thermostat, maintained at a constant temperature. The flasks were removed separately at known intervals of time and the solutions were immediately filtered. Several trials showed that the effective filtration can be quickly carried out through filter papers coated with a thin layer of collodion. The filtrate was then made up to 100 c.c. and the dichromate formed was estimated by titrating it against a standard solution of the ferrous ammonium sulphate, using diphenylamine as the indicator.

The results in Table I show that the presence of chromium sulphate does not affect the estimation of dichromate ions by the method mentioned above. It will be noticed that the mixtures chosen contain very large proportions of chromium sulphate as it happens in actual experiments.

<div align="center">TABLE I.</div>

10 C.c. of the $K_2Cr_2O_7$ solution $\equiv 9\cdot5$ c.c. of a solution of ferrous am.sulphate.

Mixtures		Ferrous ammonium sulphate.	
$K_2Cr_2O_7$.	$Cr_2(SO_4)_3$.	Reqd.	Calc.
6 c.c.	44 c.c.	5·65 c.c.	5·70 c.c.
4	46	3·80	3·80
2	48	1·90	1·90
1	49	0·95	0·95

The results obtained are given in the following tables in which C represents the concentration of chromium sulphate solution in the form mentioned above; y, the equivalents of dichromate ions formed at various intervals and T, the temperature at which the reaction was carried out.

<div align="center">TABLE II.</div>

<div align="center">Particles between 60 and 80 mesh.</div>

Time.	Equivalents of dichromate ions formed			
	($C = 61\cdot6 \times 10^{-4}N$)		($C = 154\cdot0 \times 10^{-4}N$)	
	$T = 46°$.	$T = 36°$.	$T = 46°$.	$T = 36°$.
2 min.	$6\cdot05 \times 10^{-4}$	$4\cdot29 \times 10^{-4}$	$8\cdot53 \times 10^{-4}$	$5\cdot90 \times 10^{-}$
5	8·25	5·89	10·45	7·50
10	10·45	6·97	12·10	9·11
20	11·55	7·77	14·03	9·91
30	11·83	8·31	14·58	10·45
40	12·93	9·38	15·13	10·99
60	14·58	10·18	15·95	1·80

TABLE III.

Particles between 80 and 100 mesh.

Time.	Equivalents of dichromate ions formed.		
	$C = 61 \cdot 6 \times 10^{-4} N$		$C = 154 \cdot 0 \times 10^{-4} N$
	$T = 46°.$	$T = 36°.$	$T = 46°.$
2 min.	$7 \cdot 15 \times 10^{-4}$	$4 \cdot 95 \times 10^{-4}$	$10 \cdot 45 \times 10^{-4}$
5	$8 \cdot 80$	$6 \cdot 88$	$12 \cdot 38$
10	$11 \cdot 00$	$7 \cdot 98$	$13 \cdot 48$
20	$13 \cdot 20$	$9 \cdot 63$	$15 \cdot 13$
30	$13 \cdot 75$	$10 \cdot 73$	$15 \cdot 68$
40	$14 \cdot 58$	$11 \cdot 00$	$16 \cdot 23$
60	$15 \cdot 68$	$11 \cdot 53$	$17 \cdot 33$

DISCUSSION.

It will be seen that the reaction between chromic sulphate and manganese dioxide is very rapid in the beginning but slows down within a short time. Tables I and II give the effects of (i) the change in concentration of chromium sulphate, (ii) the size of the particles, roughly indicated by the size of the sieves through which the manganese dioxide has been sieved, and (iii) the temperature on the reaction. It will be seen that increasing amounts of dichromate ions are formed as (a) the concentration of the chromic sulphate solution, (b) the size of the particles, and (c) the temperature at which the reaction is carried out, are increased.

Nernst (Z. physikal. Chem., 1904, 47, 52) has shown on certain assumptions that the order of heterogeneous reactions which proceed fairly rapidly is unimolecular. This conclusion has been verified mainly in dissolution reactions (cf. Von Name, Amer. J. Sci., 1917, 43, 453; King and Braverman, J. Amer. Chem. Soc., 1932, 54, 1744; Collenberg and Bodfross, Z. physikal. Chem., 1921, 101, 117). Attempts made to determine the order of the reaction studied in this investigation showed that it is not a unimolecular one.

The heterogeneous reactions take place owing to the adsorption of the molecules of the reactant at the surface of a solid. The rate of this reaction is retarded if the molecules of the product or products formed in the reaction are also adsorbed by the solid. In the heterogeneous reactions at the gas-solid interface, if the adsorption of the reacting gas is smaller

than the adsorption of the gaseous product, the rate of reaction is given by

$$\frac{dx}{dt} = \frac{k(a-x)}{1+bx}$$

where k and b are constants. The integrated form of this expression is

$$v = \left(a + \frac{1}{b} \right) k_m - \frac{k}{b} \qquad \qquad \dots \ (1)$$

where $\qquad v = \dfrac{x}{t}$ and $k_m = \dfrac{2 \cdot 3}{t} \ \log \ \dfrac{a}{a-x}$.

Hinshelwood and Prichard (*J. Chem. Soc.*, 1925, **127**, 327) found that the above expression is applicable to the catalytic decomposition of nitrous oxide at the surface of platinum. On plotting v against k_m they found that the curve is a straight line which cuts the axis of v on the negative side and the slope of the line is given by $\left(a + \dfrac{1}{b} \right)$.
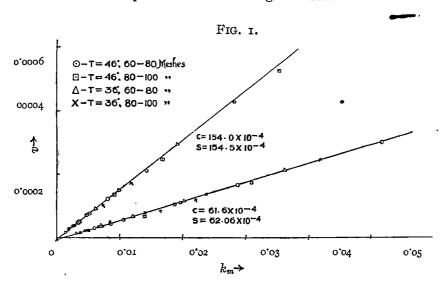
If the adsorption of the gaseous product is very great then the reaction velocity is given by

$$\frac{dx}{dt} = \frac{k(a-x)}{x}$$

which, on integration, gives

$$v = ak_m - k. \qquad \qquad \dots \ (2)$$

The application of this expression has been realised by Hinshelwood and Burk (*J. Chem. Soc.*, 1925, **127**, 1114) in the decomposition of ammonia on the surface of heated platinum wire in the region of 1000°.

FIG. 1.

The application of the expressions (1) and (2) was examined in the case of the reaction between chromium sulphate and manganese dioxide. Values of v are plotted against k_m and the straight lines obtained are shown in Fig 1. It will be seen that the straight lines intersect the v-axis on the negative side but the values of the intercepts are very small. Also points corresponding to the reaction at different temperatures with the solution of chromium sulphate of the same concentration and of different particle size, lie on the same straight line. Values of the slopes S of the two lines shown in the figure are nearly the same as the concentration C of the chromium sulphate solution. This leads to the conclusion that the reaction studied in this investigation is analogous to the decomposition of ammonia and that the rate of this reaction is governed by the expression (2).

Further work on the subject is in progress.

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A NEW METHOD OF PREPARING HYDROSOLS OF SHELLAC AND OTHER NATURAL RESINS AND THEIR PROPERTIES.

By Santi Ranjan Palit.

A method for the preparation of concentrated clear hydrosols of shellac, rosin, mastic, etc. has been described, and a brief study of their physico-chemical and colloidal properties has been made. The shellac sols have been found to produce thin, transparent varnish films on air-drying which are more hard and water-resistant than ordinary shellac films from French polish.

Hydrosols of resins like mastic, gamboge, shellac, etc. have been prepared and studied by a number of workers. These sols are generally prepared by the method, perhaps first used by Spring (*vide* Burton, " Physical Properties of Colloidal Solutions ", p. 18), of pouring a small quantity of alcoholic or ethereal solution of the resin in cold or boiling water and the subsequent expulsion of the organic solvent by heating. This method has the drawback that the sols are, as a rule, milky-opaque having a preponderance of coarse microscopic particles and contain a very small quantity of the dispersed phase (about 0·1 g. per litre). The present paper deals with a different method of producing transparent concentrated hydrosols of the resins and a study of their properties.

EXPERIMENTAL.

Method of Preparation.

The method, in short, consists in dialysing an ammoniacal solution of the resin when free ammonia diffuses out and the ammonium salt of the resin suffers membrane hydrolysis leading to the formation of a colloidal solution of the resin.

The resins (about 5-15 g.) were dissolved in 100 c.c. of ammonium hydroxide (0·1 — 0·5N) to a slight excess of ammonia. After filtration the solution was dialysed in thin cellophane (P. T. 300) or collodion bags against distilled water which was changed twice a day. With the progress of dialysis colloidal properties began to appear as evidenced by the ease of coagulation of the resin by the addition of $N/2$-potassium chloride to a small portion of the solution. Dialysis was continued until the dialysate

gave a slight colouration (no precipitate) with Nessler's solution and only a faint opalescence on addition of dilute hydrochloric acid or alum solution. This was achieved in about four or five days with the thin cellophane membranes (P.T. 300), and in two to three days with the collodion membranes. The criteria of formation of a good sol are that it should be transparent, neutral or very faintly acidic, and easily coagulable by the addition of about its own volume of o·5N-potassium chloride solution. If dialysis is continued for a much longer time, the sol gradually turns opalescent and becomes increasingly sensitive to electrolytes. Such over-dialysed sols either tend to form soft gel-like mass or separate coarse precipitates on keeping.

A method of further purification of the sol thus obtained, which has been found to be very suitable for the rosin sol, is to ultrafilter the sol and to treat the still moist residue on the ultrafilter with water when the residue disperses to form a faintly acidic (p_H 5 to 5·5), stable and transparent sol which shows no tendency to settle or separate any coagulum even on keeping for over six months Other alkalis like sodium carbonate or borax have also been used with success but the yield is somewhat less in these cases.

The properties of the final sol are found to depend on the initial concentrations of ammonia and the resin, and also on the rate and extent of dialysis. The sols contain ammonia to the extent of about 10 to 45% of the total equivalent of the resin acid present in the sol. This small concentration of ammonia is necessary for the stability of the sol and removed by prolonging the dialysis, the sol coarsens and ultimately coagulates on keeping. This method has been applied with success in the cases of shellac, bleached shellac, rosin, abietic acid and mastic.

Physical and Chemical Properties.

The sols thus produced are clear, transparent liquids usually having p_H values between 6·6 and 7·2 for shellac sols and between 5·0 and 5·5 for rosin sols. Due to considerable osmosis and the diffusion of the resin anions during dialysis the concentration of the final sol is much less than that originally taken, but the sols can be concentrated to any desired concentration by slowly evaporating on the water-bath, if the concentration of ammonia in the sol is not below a certain critical amount. The properties of some typical sols prepared by this method are summarised in the following table,

TABLE I.

	Shellac hydrosol.		Rosin sol.
	I	II	
1. Appearance	Transparent.	Transparent, slightly hazy in reflected light	Clear in transmitted light, opalescent in reflected light
2. Conc. of resin (g. per 100 g. of water)	3·72	3·2	0·79
3. Conc. of ammonia in the sol in normality	0·025	0·017	0·0031
4 Sp. conductivity (mhos) at 30°	$1·38 \times 10^{-3}$	$1·33 \times 10^{-3}$	$1·48 \times 10^{-4}$
5. p_H	7·23	7·10	5·42
6. Relative density (30°)	1·0058	1·0056	1·0010
7. Relative viscosity (30°)	1·30	1·24	1·04

The concentration of the resin was determined by evaporating to dryness a known weight of the sol and then heating for about 2-3 hours at 90-95° until the weight remained fairly constant. Ammonia was estimated by micro-Kjeldahl method according to the directions of Pregl " Organic · Microanalysis ". p_H values were determined with a glass electrode (Morton's type) assembled with a Cambridge valve potentiometer. All other constants in the above table were determined by the usual apparatus.

A simple calculation from the known acid values of the resins (Shellac, 70 ; Rosin, 160) shows that the stabilising electrolyte (ammonia) is present in such concentrations as to neutralise only 10-50% of the total resin acid present. In fact, the shellac sols prepared by this method are not very stable on keeping if the concentration of ammonia is not sufficient to neutralise at least 25% of the total acidity of the resin, but with rosin sols, except for a slight haziness, there is hardly any loss of stability even with concentrations of ammonia capable of neutralising only 10% of the total acidity of the rosin.

Colloidal Properties.

The sols show strong Tyndall effect, which is easily visible with illumination from a powerful source of light in a dark room.

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The sols do not pass through ultrafilters as proved by analyses of their ultrafiltrates. The results are shown in Table II. A Zsigmondy type 9 cm. ultrafilter bed with commercial ultrafilters manufactured by de Haen & Co. were used. The sols were first ultrafiltered through 'membranefilters' (fine) and then through 'ultrafilter' (fine), the latter being capable of retaining very fine colloids like gold sol, albumen, etc.

TABLE II.

	Shellac sol I		Shellac sol II.		Rosin sol.	
	Original.	Ultrafiltrate.	Original.	Ultrafiltrate.	Original.	Ultrafiltrate.
1. Residue on evaporation of 10 c.c.	0·361	0·014	0·262	0·0134	0·0786	0·004
2. Concentration of ammonia	—	—	0·0124	0·0012	0·0031	trace

Table II shows that greater part of the ammonia in the sol is present as stabilising ions in the double layer or deeply embedded in the core of the micelles and not in the inter-micellary liquid and so does not pass into the ultrafiltrate. It will be observed that for the shellac sols about 4% of the resin pass into the ultrafiltrate, which is perhaps partly due to the extremely fine state of subdivision of the dispersed phase and partly to the presence of free ammonium salt of the resin.

The sols are coagulated by electrolytes, acids being extremely active but otherwise the coagulation follows the valency rule Bases like caustic soda first precipitate the sol and then slowly dissolve the resin thus precipitated. In Table III are given the coagulation values with some typical electrolytes. These coagulation values or liminal concentrations were determined according to the procedure followed by Freundlich (Z. physikal. Chem., 1903, 44, 129) by noting the minimum concentration of the electrolytes necessary to produce visible coagulum or loss of tranparency after two hours on mixing equal volumes of the sol and the electrolyte solution. To obviate the difficulty of observing coagulation due to gel formation, all coagulation experiments were carried out with sols diluted to attain a concentration of 1% solid content for shellac and 0·1% for rosin. Aluminium chloride sometimes seemed to produce 'anomalous series' effect with shellac sols.

TABLE III.

	Liminal concentration (millimols/litre).		
Electrolytes.	Shellac sol I.	Shellac sol II.	Rosin sol.
Hydrochloric acid	1·1	0·74	1·16
Potassium chloride	240·0	190·0	250·0
Barium chloride	3·8	3·2	9·0
Aluminium chloride	1·05	0·65	0·062

The coagulation values depend on the concentration of ammonia present in the sol as shown by the values (Table IV) for different samples of the same shellac sol (A_1, A_2, A_3 and A_4) taken out after different degrees of dialysis. The sols A_1, A_2, and A_3 were transparent, while sol A_4 was slightly opalescent. The rosin sol A_2 was prepared by ultrafiltering sol A_1 and then dispersing the moist residue on the ultrafilter by addition of water when it formed a stable, transparent, non-settling hydrosol. Coagulation values were determined after dilution of the sols to 1 g. of solid content per litre. It is of interest to note from a comparison of the coagulation values of the rosin sols A_1 and A_2 that the presence of a small quantity (about 5% of the total) of ammonia in the intermicellary liquid may produce a large difference in the coagulation values.

TABLE IV.

Sol.	No. of days dialysed.	Conc. of resin g./1000 g. water.	Conc. of ammonia $\times 10^3$.	Coagulation value with KCl.
A_1 Shellac sol	4	1·0	0·801	355
A_2 ,, ,,	5	1·0	0·727	315
A_3 ,, ,,	7	1·0	0·586	215
A_4 ,, ,,	10	1·0	0·474	165
A_1 Rosin ,,	—	1·0	0·391	240
A_2 ,, ,,	—	1·0	0·372	175

Film-forming Properties.

The shellac sols have the useful property of drying to a thin transparent film at room temperature in about one or two hours. Test panels on glass

show such films to have high scratch-hardness and water resistance. These films neither show any tendency to dissolve nor blush when kept immersed in water for 24 hours, whereas films from the ordinary spirit-shellac varnish blush in about an hour. The films are harder consistent with the fact that the shellac in the sol contains more hard resin than ordinary shellac due to a more rapid diffusing of the soft resin during dialysis. In fact, the percentage of soft resin in the sol is found to vary between 8 and 12 as against 28% in the original shellac. It is suggested that ammoniacal solutions of shellac should be dialysed before application as varnish if it is desired to confer to them water-resisting properties, paler colour and high scratch-hardness.

· The author wishes to thank Dr. H. K. Sen, Director, Indian Lac Research Institute for his kind interest and helpful suggestions.

KINETICS OF THE REACTION BETWEEN POTASSIUM PERSULPHATE AND ALKYL IODIDES. PART III. CATALYTIC ACTIVITY OF A WEAK ACID.

BY M. S. TELANG AND V. V NADKARNY.

A detailed study of the hydrogen ion catalysis in the persulphate-alkyl iodide reaction is made by using a weak acid (acetic) as a source of the catalyst. The hydrogen ion concentration is controlled by the addition of neutral salts, sodium acetate and by varying the concentration of the acid itself. " Secondary electrolyte effect " is observed in presence of neutral salts. The catalytic coefficients of acetate ions and of molecules of undissociated acetic acid have also been determined. The reaction is accelerated by hydrogen and acetate ions and retarded by molecules of undissociated acetic acid.

In continuation of our previous communication (Telang and Nadkarny, *J. Indian Chem. Soc* , 1939, **16,** 536) a more extensive study of the hydrogen ion catalysis has been made by employing a weak acid like acetic acid as a source of the catalyst. Incidentally, the study of the catalysis by all ions and molecules is made.

With acetic acid as the source of the catalyst

$$K' = \frac{C_{\mathrm{H}^+} \, C_{\mathrm{A}^-}}{C_{\mathrm{HA}}} \cdot f_{\mathrm{H}^+} \, f_{\mathrm{A}^-}$$

(*vide* Moelwyn-Hughes, "Kinetics of Reactions in Solution", 1933), both activity coefficients decrease with the addition of neutral salts, so that an increase in C_{H^+} is anticipated and the " secondary salt effect " should be positive. Brönsted and La Mer (*J. Amer. Chem. Soc.*, 1924, **46,** 555) have applied these considerations to the catalytic decomposition of diazoacetic ester by hydrogen ion. Dawson and Lowson (*J. Chem. Soc.*, 1929, 393, 1217) found in the hydrolysis of ethyl acetate by means of three different acids (acetic, glycollic and dichloroacetic) in the presence of sodium chloride that the reaction velocity at first increased with increasing concentration of salt. The concentration of hydrogen ion has been obtained by means of the relation $k'' = k[\mathrm{H}^+]$, where k'' is the catalytic coefficient of Bredig and Fraenkel (*Z. Electrochem.*, 1905, **11,** 525) independent of the nature of the acid. k'' is calculated from the equation,

$ln \; k'' = 29 \cdot 27 - 17480/RT$ (Fraenkel, *Z. physikal. Chem.*, 1907, **60,** 202).

The researches of Goldschmidt (*Z. physikal. Chem.*, 1910, **70,** 627), Bredig (*Z. Electrochem.*, 1912, **18,** 535), Snethlage (*ibid.*, p. 539) and Dawson (*J. Chem. Soc.*, 1913, **103,** 2135) have indicated that the molecules

of undissociated acid as well as hydrogen ions possess definite catalytic properties. Dawson extended the hypothesis of dual catalysis by ascribing catalytic effects to all the molecular and ionic species present. The influence of acetic acid as a solvent was referred to in Part I of this series (Telang and Nadkarny, *loc. cit.*) and in view of the catalytic effects due to undissociated as well as ionised acetic acid, the influence of acetic acid on the kinetics of the persulphate-alkyl iodide reaction merited further investigation.

EXPERIMENTAL.

The reaction was carried out at 50° for two hours in each case in the manner previously described (Telang and Nadkarny, *loc. cit.*).

TABLE I.

10 C.c. of $N/5$-C_2H_5I (alcoholic) + 10 c.c. of $N/5$-$K_2S_2O_8$ + 0·5 c.c. of 0·565N-acetic acid + x c.c. of $4N$ KNO_3 made up to 100 c.c. with water.

x.	Electrolyte (added) concentration.	Titre $(N/200I_2)$.	Velocity constant $k \times 10^6$.
0·5 c.c.	0·02 N	12·3 c.c.	258·9
1·0	0·04	12·1	255·2
2·5	0·1	12·0	253·2
10·0	0·4	15·0	318·4
15·0	0·6	16·6	353·0
20·0	0·8	16·8	358·7

TABLE II

(Based on Table I). $k''_{50}° = 8·252$.

Total electrolyte concentration.	$k_{50}° \times 10^6$.	$[H^+] \times 10^5$.
0·04 N	92·7	1·12
0·06	84·0	1·018
0·12	67·0	0·812
0·42	57·2	0·693
0·62	41·8	0·507
0·82	—	—

TABLE III.

10 C.c. of $N/5$-C_2H_5I (alcoholic) + 10 c.c. of $N/5$-$K_2S_2O_8$ + 1 c.c. of glacial acetic acid + x c.c. of $4N$-$NaNO_3$ made up to 100 c.c. with water.

x.	Electrolyte concentration.	Titre.	Velocity constant $k \times 10^6$.
Nil	Nil	8·2 c.c.	172·6
0·5 c.c.	0·02 N	9·1	184·2
1·0	0·04	8·5	178.4
2·5	0·1	9·6	203·3
5·0	0·2	9·5	201·4
7·5	0·3	11·6	245·6
10·0	0·4	11·6	245·6
20·0	0·8	12·4	260·8
40·0	1·6	13·8	291·6

TABLE IV.

10 C.c. of $N/5$-C_2H_5I (in acetic acid) + 10 c.c. of $N/5$-$K_2S_2O_8$ + x c.c. of $4N$-$NaNO_3$ made up to 100 c.c. with water.

x.	Electrolyte concentration.	Titre.	Velocity constant $k \times 10^6$.
Nil	Nil	9·3 c.c.	195·6
0·5 c.c.	0·02 N	8·1	170·7
1·0	0·04	7·8	163·0
2·5	0·1	7·9	165·0
5·0	0·2	9·3	195·6
10·0	0·4	9·5	201·4
20·0	0·8	10·3	216·8

TABLE V.

10 C.c. of $N/5$-C_2H_5I (alcoholic) + 10 c.c. of $N/5$-$K_2S_2O_8$ + x c.c. of buffer made up to 100 c.c. with water. The buffer consisted of 25 c.c. of 0·565 N-acetic acid + 75 c.c. of $1N$-Na-acetate in a total volume of 100 c.c. of buffer.

x.	Titre.	Acetate ion concentration.	Velocity constant $k \times 10^6$.
0·5 c c.	10·6 c.c.	0·0038 N	222·5
1·0	9·7	0·0075	205·2
2·5	8·4	0·0188	176·5
5·0	10·0	0·0375	211·0
10·0	10·4	0·075	218.7
15·0	12·7	0·1125	268·5
20·0	14·2	0·150	301·1
40·0	18·8	0·30	400·9

TABLE VI.

10 C.c. of $N/5$-C_2H_5I (alcoholic) + 10 c.c. of $N/5$-$K_2S_2O_8 + x$ c.c. of buffer made up to 100 c.c. with water. The buffer consisted of 50 c.c. of $0.565N$-acetic acid + 50 c.c. of $1N$-Na-acetate in a total volume of 100 c.c. of buffer.

x.	Titre.	Acetate ion concentration.	Velocity constant $k \times 10^6$.
0.5 c.c.	11.0 c.c.	0.0025 N	232.1
1.0	9.1	0.005	184.2
2.5	9.2	0.0125	193.7
5.0	8.6	0.025	180.3
10.0	9.7	0.05	205.2
15.0	10.3	0.075	216.8
20.0	10 8	0.10	228.2
40.0	14.4	0.20	305.0

TABLE VII.

10 C.c. of $N/5$-C_2H_5I + 10 c.c. of $N/5$-$K_2S_2O_8$ + 5 c.c. of $0.565N$-acetic acid + x c.c. of $1N$-Na-acetate made up to 100 c.c. with water.

x.	Titre.	Acetate ion concentration.	Velocity constant $k \times 10^6$.
0.5 c.c.	10.4 c.c.	0.005 N	218.7
1.0	9.5	0.01	201.4
2.5	8.8	0.025	186.1
5.0	10.1	0.05	193.7
10.0	11.6	0.10	245.6
15.0	13.5	0.15	285.9
20.0	14.5	0.20	306.9
40.0	23.95	0.40	514.0

TABLE VIII.

10 C.c. of $N/5$-C_2H_5I (alcoholic) + 10 c.c. of $N/5$-$K_2S_2O_8 + x$ c.c. of $0.565N$-acetic acid made up to 100 c.c. with water.

x.	Titre.	Velocity constant $(k \times 10^6)$.	Concentration of the acid (c).	$\sqrt{c}$.	$(k/\sqrt{c}) \times 10^6$.
0.5 c.c.	11.2 c.c.	236.0	0.00284 N	0.0533	4432
1.0	7.8	163.0	0.00567	0.0753	2165
2.5	8.7	184.2	0.01418	0.1191	1547
5.0	8.6	180.3	0.02835	0.1684	1071
7.5	10.3	216.8	0.04253	0.2062	1052
10.0	10.7	226.3	0 0567	0.2381	950.4
15.0	10.4	218.7	0.08505	0.2917	749.9

D I S C U S S I O N.

Secondary Electrolyte Effect.

In Table II, it is observed that the hydrogen ion-concentration decreases steadily till it reaches the minimum value at a concentration of 0·82 H of the electrolyte. The values of $k_{50}°$ given are corrected for the catalytic effect of added KNO_3 and also for the initial reaction velocity in the absence of acetic acid catalyst. Hence neglecting the small catalytic effects of acetate ions and undissociated acetic acid molecules, the $k_{50}°$ values given represent the velocity due to hydrogen ions only. The total electrolyte concentration also includes the potassium persulphate concentration. The k values evaluated from the equation

$$k = \frac{[H^+]^2}{c - [H^+]}$$

where c is the acid concentration, also run in a similar way as the hydrogen-ion concentration. Apparently this is rather unusual in the sense that according to theory, the "secondary electrolyte effect" for acetic acid catalysis should be positive. In order to confirm the results, two more experiments were performed with higher concentrations of acetic acid and the results are given in Tables III and IV. It is seen from these tables, that the velocity increases at the first addition of salt and then begins to decrease. These observations are unlike Dawson's results where this change was observed at comparatively high salt concentrations. It may be of interest to note that the resultant velocities in this reaction tend to decrease, at first pass through a minimum and then again increase. This is probably due to the primary catalytic effect of the added electrolyte

Catalytic Coefficients of Acetate Ions and of Molecules of Acetic Acid.

k_A, the catalytic coefficient of the acetate ion and k_M, that of the undissociated molecule of acetic acid have been calculated by employing three different methods (*vide* Glasstone, "Recent Advances in General Chemistry", 1936), Chapter VIII. These terms are evaluated graphically. Experiment shows that the molecules of undissociated acid have a negative catalytic coefficient. The results obtained by all the three methods are of the same order of magnitude although the actual figures may show slight differences.

In accordance with the equation, $V = k_A x + k_M c$, if x is plotted against V, the reaction velocity passes through a fairly sharp minimum and then

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begins to increase in a linear manner as the salt concentration is increased (*vide* Table VII). The slope of this line $k_A = 0.9 \times 10^{-3}$, and its intercept when extrapolated to cut the V-axis ($x=0$), $k_M c = -2.5 \times 10^{-6}$, hence $k_M = -0.9 \times 10^{-3}$. (While calculating $k_M c$, the initial reaction velocity in the absence of the catalyst was taken into consideration).

According to the equation

$$V/\sqrt{c} = (k_H{}^+ + k_A -- k_M)\sqrt{k} + k_M\sqrt{c},$$

if $V/\sqrt{c}$ is plotted (Table VIII) against $\sqrt{c}$, a straight line representing the variation of the reaction velocity with the concentration of the acid is anti-cipated. But in this experiment it is not so. The values of $V/\sqrt{c}$ decrease rapidly at first and then gradually decrease in a linear manner with increasing $\sqrt{c}$. From this behaviour, it is clear that the hydrogen-ion concentration cannot be neglected in very dilute solutions. For purposes of evaluating the required constant, the slope of the line at higher concentrations, where the representation is a linear function, is considered. Hence the slope $k_M = -2.0 \times 10^{-3}$.

By employing equations,

$$k_A = \frac{l'q - lq'}{q - q'} \text{ and } k_M = \frac{l - l'}{q - q'},$$

$k_A = 1.35 \times 10^{-3}$, and $k_M = -1.06 \times 10^{-3}$ (Tables V and VI).

Attention may be drawn to the solvent effect of acetic acid as given in Part I (Telang and Nadkarny, *loc. cit.*). It was observed that the velocity in presence of acetic acid remained practically unaltered. The reaction is highly catalysed by hydrogen ions and the velocity in acetic acid should have increased correspondingly. Whatever acceleration may be produced by hydrogen and acetate ions may be counterbalanced by the retardation due to molecules of undissociated acetic acid. Hence, probably, no change in the reaction velocity with acetic acid as the solvent is observed.

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KINETICS OF THE SAPONIFICATION OF ESTERS IN DILUTE SOLUTIONS. A STUDY OF THE EFFECT OF SUBSTITUTION ON THE RATE-DETERMINING FACTORS.

By Hiralal Shrivastava

A kinetic study of the saponification of eleven aliphatic esters, R′COOR (where R and R′ vary from CH_3 to C_5H_{11}) has been made in pure and dilute aqueous solutions. Analysis of the results on the basis of the equation $K = PZe^{-E/RT}$ shows that changes in velocity are due in a greater measure, if not entirely, to changes in the steric factor In the case of normal esters, however, the energy of activation shows a slight but progressive increase as the series is ascended, whereas for isomeric esters the energy of activation is practically the same. These observations have been discussed in the light of the results obtained by others.

Kinetic studies of saponification of esters may be traced back for more than half a century. It is, however, only during recent years that a rational study of the subject has been attempted in the light of the application of the equation $K = PZe^{-E/RT}$ in the interpretation of kinetic data. Special attention has been directed to the experimental determination of the energy of activation, (E) as a means towards arriving at a correct understanding of the effect of alkyl substitution on the different rate-determining factors in the saponification of esters.

Earlier work on the subject in pure aqueous solutions (Warder, *Ber.*, 1881, **14**, 1361; *J. Amer. Chem. Soc.*, 1881, **3**, 203; Reicher, *Annalen*, 1885, **228**, 257; 1885, **232**, 103; 1887, **238**, 276; Smith and Olsson, *Z. physikal. Chem.*, 1922, **102**, 26; 1925, **118**, 99) shows that if we start with CH_3COOR and vary R from C_2H_5 to C_5H_{11} there is no appreciable variation in E (which is practically constant round about 11,000 cals.). More recently Evans, Gordon and Watson (*J. Chem. Soc.*, 1938, 1439) from their study of the rates of saponification of different esters in 85% alcoholic solutions found that (*i*) E increases gradually as the normal series is ascended and tends to reach constant maximum, and also (*ii*) in esters which are not branched at the α-carbon atom the changes in K are due almost entirely to changes in E. These findings have been adversely criticised by Smith and Levenson (*J. Amer. Chem. Soc.*, 1939, **61**, 1172; also *cf.*, Smith *ibid.*, p. 254) whose experimental results show no appreciable variation in E as one passes up the ester series. These latter authors contend that variations in K are due entirely to changes in the steric factor P.

In a subsequent paper Smith and McReynolds (*ibid.* p. 1963) have offered an explanation of all observed regularities and abnormalities in these saponification studies on the basis of a ring theory for the structure of higher members.

All inferences and conclusions in these matters obviously depend upon the accuracy of the kinetic measurements and the conditions under which they are made. The investigations referred to above have all been made in reaction mixtures at concentrations convenient for purposes of the usual acidimetric and alkalimetric titrations. This analytical procedure puts a limit to the dilution up to which we can proceed.

It appeared to the author desirable to undertake a study of the kinetics of saponification of a series of esters in very dilute solutions with a view to collecting accurate data and testing the validity of the different views put forward in regard to the influence of substitution on the rate of reaction. The present study deals with kinetic measurements of the saponification of eleven esters.

EXPERIMENTAL.

Preparation and Purification of Esters.

Ethyl propionate, *n*-propyl acetate, *iso*propyl acetate and butyl acetate were prepared by Fischer-Speier's method from the corresponding (Kahlbaum's) alcohols and acids. Other esters were purchased from Kahlbaum. Each ester was shaken with a slight excess of dilute sodium carbonate solution to remove any acid present, then washed with pure water, and dried thoroughly by shaking with anhydrous sodium sulphate and leaving overnight. The purified and dried ester was repeatedly distilled. In the case of low boiling esters, an eighteen-inch fractionating column was used. In every case the middle fraction distilling over at a constant head temperature was collected for experimental work. The observed boiling points are recorded below. The figures within brackets indicate the corresponding pressures in mm. of mercury :—Methyl acetate, 56·2° (738·40) ; ethyl acetate, 76·0° (735·65) ; *n*-propyl acetate, 100·5° (739·35) ; *iso*propyl acetate, 88·0° (734·15) ; *n*-butyl acetate, 125·0° (739·35) ; *iso*amyl acetate 137·5° (738·70) ; methyl propionate, 78·5° (738·70) ; ethyl propionate, 98·0° (734·15) ; methyl butyrate, 101·0° (735·35) ; ethyl butyrate, 118·5° (735·35) ; ethyl *iso*valerate, 133·2° (736·20).

The purified esters were analysed by leaving overnight a weighed sample of each ester in contact with a known excess of standard alkali in well stoppered Jena glass flasks, and then titrating the excess of alkali with standard acid. All the esters gave satisfactory proof of purity (between 99·5 and 100%).

Analytical Procedure and other Experimental Details.

The saponification was studied in aqueous potassium hydroxide solutions at three or four temperatures for each ester. An electrically controlled water thermostat was used and the temperature could be kept constant to ±0·01 of a degree. All solutions were prepared in conductivity water. Vessels used were of Jena or pyrex glass.

The main difference between previous studies and this one is chiefly in regard to the dilution at which measurements have been made, dilution herein employed being in the region of 0·005N to 0·001N.

The reaction was followed by pipetting out known volumes of the reaction mixture at different intervals of time and running it into a known quantity of hydrochloric acid solution. This stopped the reaction, the acid catalysed hydrolysis being comparatively very slow. The excess of acid was estimated by adding to the mixture potassium iodide and potassium iodate and titrating the iodine liberated against standard (nearly 0·005N) sodium thiosulphate solution. This iodometric method, as is well known, is capable of yielding accurate results and has enabled us to extend our studies to the region of great dilutions.

In the case of low boiling esters the reaction mixture was made up by diluting 25 c.c. of 0·04N-potassium hydroxide solution to 225 c.c. with conductivity water, and then adding in 25 c.c. of a freshly prepared ester solution of known concentration (in the neighbourhood of 0·04N) at the required temperature. In order to reduce to a minimum losses due to evaporation, the ester solution was prepared as follows : a 100 c.c measuring flask was filled with water to within a short distance of the mark on the neck. The ester was then added and dissolved by shaking well. Only a few drops of water were then needed to dilute the solution to the mark. In the case of high boiling esters, the ester was directly added to the alkali solution at the required temperature from an accurately calibrated micro-pipette.

At least two, and usually three or four runs were made at each temperature for each ester.

The bimolecular velocity constant was calculated in terms of litres/g. mols. min. from the equation

$$\log K = \frac{2 \cdot 303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

RESULTS.

The results of a typical run are given in Table I.

TABLE I.

Saponification of ethyl acetate at 25°.

$(N/252\cdot29$ ester $+ N/250\cdot1$KOH$)$; $(a-b)=0\cdot181$ c.c. $N/208\cdot22$; $(a-x)$ and $(b-x)$ are expressed in c.c. $N/208\cdot22$.

Time (t)	Alkali conc. (a−x)	Ester conc. (b−x)	Velocity constant, K. (in litres/g. mols. min)
o min	16·875	16·694	—
4	15·85	15·669	5·4606
9	14·675	14·494	5·3685
15	13·425	13·244	5·4713
22	12·20	12·019	5·5301
32	10·90	10·719	5·4225
		Mean	5·4500

TABLE II.

Effect of variation in initial concentration of alkali and ester on the velocity constant for the ethyl acetate by aqueous KOH at 28°.

Initial conc. of KOH.	Initial conc. of ester.	$K_{28}°$ (litres/g. mols. min.).
0·004 N	0·005 N	6·89
,,	0·00125	6·72
0·0025	0·005	6·825
,,	0·0025	6·865
0·002	0·005	6·818
0·001	0·010	6·355
,,	0·005	6·22
,,	0·002	6·16
,,	0·001	5·87

The figures in Table II show that when the initial concentrations of the reactants are altered over a narrow range (cf. figures in the first five horizontal rows) there is no appreciable change in K. This result is in

agreement with the observations of previous workers (Arrhenius, *Z. physikal. Chem.*, 1887, 1, 110 ; Burgarsky, *ibid.*, 1891, 8, 398). The last four sets of figures (horizontal rows) show, however, that when the concentration of KOH is kept constant and the initial concentration of ester varied from 0·01M to 0·001M, the value of K falls by about 10%. Changes of such magnitude are usually met with in reactions taking place between neutral molecules and ions and an increase in K with an increase in the initial concentration of the non-electrolyte is from general considerations attributable to increase in the activity of the reacting ion. The evidence for such a view should, however, be regarded as qualitative (Moran and Lewis, *J. Chem. Soc.*, 1922, 121, 1620; Kappanna and Shrikhande, *J. Indian Chem. Soc.*, 1931, 8, 557) and the point has not been further pursued in this investigation.

Table III gives the values of K for different esters at different temperatures. These are the results of experiments carried out with different esters, the initial concentration of each reactant in the different reaction mixtures being in the neighbourhood of $M/250$. The results with different esters, therefore, relate strictly to comparable conditions—a point of importance from the standpoint of the present investigation.

Table IV contains the values of K at 25° for each ester together with the corresponding values of E, Z, PZ and P. The energies of activation were calculated from the plot of log K against $1/T$. Z was calculated from the usual kinetic theory formula in terms of litres/g. mols. min.. For this purpose the molecular diameters, σ, were calculated from Sugden's parachor values by means of the formula $\sigma = 0·725 \times 10^{-8} \times (\text{Parachor})^{\frac{1}{3}}$. The values of PZ and P were then calculated from the formula $K = PZe^{-E/RT}$.

TABLE III.

Ester.	$K_{25°}$	$K_{30°}$	$K_{35°}$	$K_{40°}$	$K_{45°}$	$K_{55°}$
Methyl acetate	8·889	11·92	15·41	19·75	—	—
Methyl propionate	7·203	10·00	13·55	18·09		
Methyl butyrate	4·860	6·456	8·992	—	14·48	24·69
Ethyl acetate	5·454	—	9·448	—	16·18	28·24
Ethyl propionate	4·588	—	8·123	—	14·015	
Ethyl butyrate	2·405	—	4·573	—	7·874	13·22
Ethyl *iso*valerate	0·871	—	1·487	—	2·397	3·818
n-Propyl acetate	4·474	—	8·054	—	13·82	
*iso*Propyl acetate	1·383	—	2·462	—	4·394	
Butyl acetate	3·863	—	7·028	—	12·11	
*iso*Amyl acetate	3·195	—	5·836	—	9·241	15·89

TABLE IV.

Ester.	K_{25}.	E.	$Z \times 10^{-8}$.	$PZ \times 10^{-8}$.	P.
Methyl acetate	8·889	10000	1·2474	1·8769	1·547
Ethyl acetate	5·454	10250	1·3817	1·7418	1·2624
n-Propyl acetate	4·474	10550	1·3987	2·3922	1·7095
isoPropyl acetate	1·383	10800	1·3759	1·1268	0·8189
Butyl acetate	3·863	10800	1·3977	3·1471	2·2517
isoAmyl acetate	3·195	10060	2·1586	0·7406	0·3447
Methyl propionate	7·203	11150	1·3856	10·744	7·777
Ethyl propionate	4·588	10400	1·3899	1·928	1·387
Methyl butyrate	4·860	10500	1·8666	2·3559	1·263
Ethyl butyrate	2·405	10700	1·7127	1·712	1·0451
Ethyl isovalerate	0·871	9600	2·1442	0·09376	0·0437

An examination of these tables reveals the following points :—

(a) K is of the same order of magnitude thus showing that the mechanism of saponification reaction is the same for different esters.

(b) K decreases at first rapidly, then slowly as the homologous series is ascended, and the value of E, in general, shows a progressive increase. But the drop in K in passing from methyl (or ethyl) propionate to methyl (or ethyl) butyrate is much greater than the decrease in K in passing from mtehyl (or ethyl) acetate to methyl (or ethyl) propionate. But there is no corresponding discrepancy between the values of K for ethyl, n-propyl, and butyl acetates; decrease in K is regular if the alcohol radical is changed.

(c) Isomeric normal esters are saponified at much the same rate; but the iso- isomer is saponified much more slowly than the n- isomer. The value of E for all isomeric esters is the same within experimental error.

(d) The value of the steric factor, P, is much smaller for esters branched at the α-carbon atom than for the normal esters, and this is paralleled by the lower values of K for these branched chain esters.

D I S C U S S I O N.

The independence of K of the initial concentration of either the ester or the alkali indicates that the reaction is a straight forward bimolecular

reaction taking place in accordance with the generally accepted mechanism for alkaline hydrolysis of esters,

$$R'\cdot C\overset{O}{\underset{OR}{\diagdown}} + \overset{\ominus}{OH} \rightleftharpoons R'-C\overset{\overset{\ominus}{O}}{\underset{OR}{\diagup}}-OH \rightarrow R'\cdot CO\cdot \overset{\ominus}{O} + R'OH.$$

It is assumed that the hydroxyl ion gets attached to the carboxyl carbon atom with the simultaneous transfer of the negative charge on to the carbonyl oxygen and the transition complex so obtained then decomposes to give the reaction products.

As the life of this transition complex is assumed to be short, the rate of reaction is determined by the rate of formation of this complex. Hence the decrease in the value of K on ascending the homologous series leads to the conclusion that as R and R' increase in size, the formation of the intermediate complex is retarded by some means. But as the value of Z does not vary appreciably with increasing length of carbon chain, this retardation may be due either to an increase in the energy of activation or to greater screening of the carboxyl group from the approach of the hydroxyl ion due to spatial disposition of the substituents R and R' or to both.

Comparatively low values of P for the esters, branched at the α-carbon atoms, show that in these cases at least, it is the steric factor which is responsible for the low velocities of saponification. Evans and co-workers attribute this to the formation of a hydrogen bond between the carbonyl oxygen and the β-carbon atom of the alkyl chain (which does not influence E perceptibly) simultaneously with the approach of the negative hydroxyl ion. This seems to be the most plausible explanation. The hydrogen bond leads to the completion of a five-membered ring and the formation of this ring naturally decreases the solid angle for the approach of hydroxyl ions to the carboxyl carbon, and thus decreases the rate of formation of the transition complex which determines K.

The formation of a similar ring structure in the butyric acid molecule (as has been suggested already by Smith and others) would offer an easy explanation of the observation that the difference between the values of K for methyl (or ethyl) propionate and methyl (or ethyl) butyrate is much larger than the difference between the values of K for methyl (or ethyl) acetate and methyl (or ethyl) propionate.

In the case of normal esters also the value of PZ changes from ester to ester, but at the same time a progressive, though slight, increase in the value of E with increasing chain length is at once evident from the

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results tabulated above. It may be argued that these variations may be only apparent and may be easily accounted for by slight experimental errors as in fact almost all the values of E lie within the range 10400 ± 400 cals. But it is somewhat remarkable that the increase is almost regular. This makes it desirable to take into account the variations in K from ester to ester.

The general conclusion is that the length and structure of the carbon chain in alkyl esters may have an effect not only on the steric factor but also on the energy of activation. In the case of early members of normal alkyl esters, variation in K seems to be due not only to a change in the steric factor but also to a progressive increase in the energy of activation. But in the case of esters branched at the α-carbon atom, the steric factor seems to be predominant. Hinshelwood and Legard (*J Chem. Soc.*, 1935, 587, 1588) demonstrated that substitution in the α-position often caused an increase in the activation energy. While this was found to be the case for the ethyl ester of *iso*valeric acid (amongst those of some other acids) studied by Evans and co-workers, the present work, in fact, shows a decrease in the value of E for ethyl *iso*valerate.

THE INTERACTION BETWEEN POTASSIUM META-PERIODATE AND THE SOLUBLE SALTS OF METALS OF ALKALINE EARTHS.

By R. K. Bahl and Manohar Lal.

On boiling a solution of potassium metaperiodate, KIO_4, with the soluble salts of the alkaline earths, the corresponding dimesoperiodates in hydrated form are precipitated. These are octahydrated calcium dimesoperiodate, $Ca_2I_2O_9$, $8H_2O$, octahydrated strontium dimesoperiodate, $Sr_2I_2O_9$, $8H_2O$ and tetrahydrated barium dimesoperiodate, $Ba_2I_2O_9$, $4H_2O$.

Bahl and Singh (*J. Indian Chem. Soc.*, 1939, **16**, 375) obtained the mesoperiodates of the rare earths by boiling disodium paraperiodate $Na_2H_3IO_6$ with an excess of soluble salts of the corresponding rare earths. Partington and Bahl (*J. Chem. Soc.*, 1934, 1771) studied the reaction of the same sodium salt with the soluble salts of the metals of the alkaline earths. Their results show that no definite strontium compound is formed, while calcium yields tetrahydrated calcium dimesoperiodate, $Ca_2I_2O_9$, $4H_2O$, and the barium salt $2\cdot3BaO\cdot I_2O_7$, $3H_2O$.

In the present work the interaction between potassium metaperiodate, KIO_4 (obtained by passing chlorine gas through a boiling solution of potassium hydroxide in the presence of iodine) and an excess of the soluble salts of the alkaline earth, has been investigated. It is found that calcium, strontium and barium form octahydrated calcium dimesoperiodate, $Ca_2I_2O_9$, $8H_2O$, octahydrated strontium dimesoperiodate, $Sr_2I_2O_9$, $8H_2O$, and tetrahydrated barium dimesoperiodate, $Ba_2I_2O_9$, $4H_2O$ respectively.

EXPERIMENTAL.

A hot solution of potassium metaperiodate, KIO_4, was added to a boiling solution of the chlorides of the corresponding alkaline earth. A white precipitate was formed in each case. For the precipitate of strontium salt prolonged heating was found necessary. The precipitates were filtered, washed, dried in an electric air oven at $40°$ and then analysed.

Alkaline earth was determined as the corresponding sulphate. Iodine and the available oxygen were estimated by the methods adopted by Partington and Bahl (*loc. cit.*).

Analytical Results.

Calcium salt, $Ca_2I_2O_9$, $8H_2O$.

Sample	Calcium.		Iodine.		Available oxygen.	
	Found.	Calc.	Found.	Calc.	Found.	Calc.
1.	12·20%	12·88%	41·11%	40·90%	17·86%	18·03%
2.	12·40		41·11		17·90	
3.	12·20		41·20		17·93	

Strontium salt, $Sr_2I_2O_9$, $8H_2O$.

1.	25·09	24·43	34·89	35·40	15·50	15·60
2.	24·80		35·00		15·50	
3.	24·84		35·14		15·50	

Barium salt, $Ba_2I_2O_9$, $4H_2O$.

1.	36·22	37·88	34·90	34·10	15·20	15·30
2.	36·40		34·65		15·20	
3.	36·24		34·70		15·20	

From the above it appears that it is not necessary that the same kind of periodate should be formed by double decomposition. Thus potassium metaperiodate, KIO_4, and disodium paraperiodate, $Na_2H_3IO_6$, on boiling with the soluble salts of alkaline earth do not form the corresponding periodates but they yield dimesoperiodates.

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THE ACTION OF CHLORINE ON THE HYDROXIDES OF ALKALINE EARTHS IN THE PRESENCE OF IODINE. PART II.

By R. K. Bahl and Surjit Singh.

By passing chlorine through hot solutions of iodine in the hydroxides of the alkaline earth the corresponding iodates in hydrated form are precipitated in each case. There is no formation of periodate by the above method.

It has been found that on passing chlorine through a boiling solution of iodine in the hydroxides of alkali metals, *e.g.*, lithium, sodium and potassium, the corresponding periodates are formed (*J. Indian Chem. Soc.*, 1940, 17, 167). This reaction has been studied in the case of the hydroxides of the alkaline earths, which have been found to yield the corresponding iodates and not the periodates. The hydroxides of calcium, barium and strontium yielded hexahydrated calcium iodate, $Ca(IO_3)_2, 6H_2O$ and monohydrated barium iodate, $Ba(IO_3)_2, H_2O$ respectively. They are all white crystalline powders.

EXPERIMENTAL.

Iodine was dissolved in a solution of the respective hydroxides (calcium hydroxide being very sparingly soluble, was taken in the form of a suspension) and heated to boiling. A white precipitate was formed in the case of barium hydroxide, a lesser amount in case of calcium hydroxide and only a milkiness appeared with strontium hydroxide. A brisk current of chlorine was then passed through the respective hot solutions of iodine in the hydroxides. There was an immediate liberation of iodine from calcium hydroxide and barium hydroxide solutions with a noticeable increase in the amount of the precipitate. In the case of strontium hydroxide there was a separation of a white precipitate followed by the liberation of free iodine. From this it appears that only a very slight amount of iodate is formed before the passage of chlorine through the solution. Chlorine takes an active part in the precipitation of strontium iodate.

In all cases most of the iodine escaped in the form of vapours and on passing more of the chlorine the solution became clear, leaving a white precipitate. It was filtered, washed and dried at 40° in the electric air oven and analysed.

Alkaline earth was determined as the corresponding sulphate. Iodine was estimated by the method given by Scott ("Standard Method of Chemical

Analyses", 1926, Vol. I, p. 244) and oxygen by Partington and Bahl's method (*J. Chem. Soc.*, 1934, 1088).

<center>TABLE I.</center>

<center>*Calcium salt.*</center>

Sample.	Calcium.	Iodine.	Available oxygen.
1	8·257%	50·928%	16·135%
2	8·154	51·341	16·762
3	8·593	50·863	16·463

These results agree with the formula $Ca(IO_3)_2$, $6H_2O$, for which the calculated value of calcium and iodine are 8·030 and 51·004% respectively. According to $2Ca(IO_3)_2, 6H_2O = 2CaO + 2I_2 + 5O_2 + 12H_2O$ available oxygen is 16·065%.

This salt was also prepared by Millon (*Ann. chim. phys.*, 1843, **9**, 413) who obtained it by crystallising a mixture of a solution of calcium nitrate or chloride with iodic acid.

<center>TABLE II.</center>

<center>*Strontium salt.*</center>

Sample.	Strontium.	Iodine.	Available oxygen.
1	19·086%	56·087%	17·187%
2	19·007	56·143	17·778
3	19·434	56·893	17·096

These values correspond with the formula of monohydrated strontium iodate, $Sr(IO_3)_2$, H_2O, the calculated values of strontium and iodine being 19·236 and 55·756% respectively. The available oxygen according to the decomposition $2Sr(IO_3)_2, H_2O = 2SrO + 2I_2 + 5O_2 + 2H_2O$ is 17·560%.

This salt was also obtained by Rammelsberg (Mellor, "A Comprehensive Treatise in Inorganic and Theoretical Chemistry", 1922, Vol. II, p. 348) by mixing together hot solutions of strontium chloride and sodium iodate.

<center>TABLE III.</center>

<center>*Barium salt.*</center>

Sample.	Barium.	Iodine.	Available oxygen.
1	27 661%	52·040%	16·201%
2	27·412	52·395	16·134
3	27·468	51·873	16·062

The values correspond with the formula Ba $(IO_3)_2$, H_2O, the calculated values of barium and iodine being 27·182 and 52·043% respectively. The available oxygen according to the equation $2Ba(IO_3)_2, H_2O = 2BaO + I_2 + 5O_2 + 2H_2O$ is 15·830%.

Gay Lussac (cf. Mellor, loc. cit.) obtained the monohydrated barium iodate, Ba $(IO_3)_2$, H_2O by merely dissolving iodine in baryta water. From this it is evident that chlorine has no further action on this solution.

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SYNTHESIS OF LOCAL ANAESTHETICS. PART IV.

By K. N. Gaind, Jnanendra Nath Ray and Jayant N. Yajnik.

Some piperidino- and diethylamino-acetyl and propionyl amines have been prepared and their local anaesthetic properties studied.

Percaine, the hydrochloride of β-diethylaminoethylamide of 2-butoxy-quinoline-4-carboxylic acid has potent local anaesthetic activity (*cf.* Jones, "Anaesthesia and Analgesia ", 1930, **2** 218; Keyes and Mclellan *J. Amer. Med. Assoc.*, 1931, **96**, 2086, Rosenstein, *Deutsch. Med. Wochenschr.*, 1929, **55**, 2010, etc.). All these workers have found percaine to be one hundred times more effective on rabbit's cornea. Hoffer (*Klin. Woch.*, 1929, **8**, 1249) finds that this drug is twelve times more effective than cocaine clinically. It is also stated to be twenty and ten times more powerful than novocaine and tutocaine respectively. It possesses a further advantage in that its solutions may be sterilised by boiling without loss of activity. On the other hand, it has a fairly high degree of toxicity (Freund, *Klin. Woch.* 1929, **8**, 1444).

Apart from the clinical advantages of this drug there is a theoretical interest in that it has typical ester grouping in the molecule replaced by an amide grouping. It appeared of interest to us to synthesise simple amides and see if any local anaesthetic properties develop in such compounds. Nirvanine (4-dimethylaminoacetyl-2-carbomethoxy-phenol) is a local anaesthetic belonging to the amide class but the typical ester grouping of cocaine is present in the molecule.

We decided to synthesise simple amides of the general formula (I).

(I)

The substances where R=OMe, OEt etc., $n=1$ or 2, $R_1=R_2=Et$ or NR_1R_2 replaced by piperidino, have been prepared and some compounds have been found to have some local anaesthetic action as determined by the rabbits' cornea method. The position of R in the nucleus with respect to the side-chain has also been varied and the results obtained have been recorded in the experimental sequel.

Experimental.

ω-*Piperidinoacetyl-o-phenetidine* (I, R=OEt in *ortho* position, R_1, R_2 replaced by piperidine and. $n=1$).—To ω-chloroacetyl-o-phenetidine (m.p.

64°, *cf. J. Amer. Chem. Soc.*, 1919, **41**, 1452) (2 g.) dissolved in dry benzene was added piperidine (2 c.c.) and the mixture refluxed for 4-5 hours on the steam-bath. After the precipitated solids were collected the solvent was removed from the filtrate and the residual oil solidified on cooling. After washing with water, it was crystallised from hot dilute alcohol, m.p. 98°. (Found: N, 10·45. $C_{15}H_{22}O_2N_2$ requires N, 10·61 per cent). The *hydrochloride,* prepared with ethereal hydrogen chloride in dry ether solution, crystallised from a mixture of acetone and ether, m.p. 158°.

ω-*Diethylaminoacetyl-o-phenetidine,* prepared in an analogous manner with diethylamine in place of piperidine, was obtained as an oil which was converted into the *hydrochloride* which was then crystallised from a mixture of acetone and ether, m.p. 118°. (Found: N, 9·39; Cl, 12·5. $C_{14}H_{22}O_2N_2,HCl$ requires N, 9·7 ; Cl, 12·3 per cent).

β-*Chloropropionyl-o-phenetidine.*—To a cooled solution of *o*-phenetidine (5 g.) in glacial acetic acid (20 c.c.) mixed with a saturated solution of sodium acetate in water (20 c.c.), was added β-chloropropionyl chloride (4·6 g.). After standing for some time in the ice-bath, the mixture was poured into a large volume of water and the precipitate collected and crystallised from alcohol, m.p. 77°. (Found : N, 6·29. $C_{11}H_{14}O_2NCl$ requires N, 6·15 per cent).

β-*Piperidinopropionyl-o-phenetidine* (I, R=OEt in *ortho* position, $n=2$, NR$_1$R$_2$ replaced by piperidine) was prepared from the foregoing compound in benzene solution by the method described before with a benzene solution of piperidine. The product was an oil; hence it was converted into the hydrochloride in the usual way and the hydrochloride crystallised from a mixture of acetone and ether, m.p. 102°. (Found: N, 8·7. $C_{16}H_{24}O_2N_2$, HCl requires N, 8·9 per cent).

The related β-*diethylaminopropionyl-o-phenetidine hydrochloride,* prepared in an analogous way with diethylamine, had m.p. 126° after crystallisation from acetone and dry benzene. (Found: N, 9·62. $C_{15}H_{24}O_2N_2$, HCl requires N, 9·33 per cent).

The *hydrochloride* of ω-*piperidinoacetyl-m-phenetidine,* prepared as described before, had m.p. 159°. (Found:. N, 8·96. $C_{15}H_{22}O_2N_2,HCl$ requires N, 9·03 per cent).

ω-*Diethylaminoacetyl -m-phenetidine hydrochloride* had m.p. 180° after crystallisation from alcohol and acetone. (Found : N, 9·74. Calc. N, 10·2 per cent).

β-*Chloropropionyl - m - phenetidine* had m.p. 80-81°. β-*Piperidino-propionyl-m-phenetidine hydrochloride,* prepared in the usual way, had m.p.

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244°. (Found : N, 10·9. Calc. N, 10·7 per cent.) and β-diethylamino-propionyl-*m*-phenetidine hydrochloride was an undistillable liquid.

ω-*Piperidinoacetyl*-p-*phenetidine*, prepared similarly to the related *ortho* compound, had m.p. 67° after crystallisation from petroleum ether. (Found : N, 10·7. Calc. N, 10·8 per cent).

ω-*Diethylaminoacetylphenetidine hydrochloride* had m.p. 154° after crystallisation from acetone and ether. (Found : N, 9·78. Calc. N, 9·77 per cent).

β-*Chloropropionyl* - ρ - *phenetidine* had m.p. 123° after crystallisation from alcohol. (Found : N, 6·4. Calc. N, 6·2 per cent). β-*Piperidino-propionyl* -p- *phenetidine* had m.p. 96° after crystallisation from petroleum ether. (Found : N, 10·16. Calc. N, 10·15 per cent). The hydrochloride had m.p. 199° after crystallisation from acetone-ether mixture.

The compounds enumerated in Table I were prepared in an analogous manner.

TABLE I.

		M.p.	Nitrogen	
			Found.	Calc.
1.	Hydrochloride of β-diethylaminopropionyl-*p*-phenetidine (ex-acetone-dry ether)	119°	9·34%	9·31%
2.	Hydrochloride of β-piperidinoacetyl-*o*-anisidine (ex-a mixture of acetone and benzene)	104°	9·84	9 84
3.	Hydrochloride of diethylaminoacetyl -*o*-anisidine (ex-benzene)	171°	14·52	15·0
4.	Hydrochloride of β-piperidinopropionyl-*o*-anisidine (ex-acetone-ether)	184°	9·84	9·7
5.	Picrate of β-diethylaminopropionyl-*o*-anisidine (ex-benzene)	173°	14·74	14·82
6	Hydrochloride of β-N-piperidinoacetyl-*m*-anisidine (ex-acetone)	154°	9·84	9·96
7.	Hydrochloride of diethylaminoacetyl-*m*-anisidine (ex-acetone)	144°	10·26	10·27
8	Chloropropionyl-*m*-anisidine (ex-petroleum ether)	92°	6·94	6·54
9.	Hydrochloride of β-N-piperidinopropionyl-*m*-anisidine (ex-acetone)	194°	9·04	9·31
10.	Hydrochloride of diethylaminopropionyl-*m*-anisidine (ex-benzene)	128°	14·66	14·61
11.	Hydrochloride of ω-N-piperidinoacetyl-*p*-anisidine (ex-acetone)	160°	9·54	9·84
12.	Hydrochloride of ω-diethylamino-*p*-anisidine-(ex-alcohol-ether)	190°	10·07	10·29
13.	β-Chloropropionyl-*p*-anisidine (ex-alcohol)	124°	6·7	6·6
14.	β-Piperidinopropionyl-*p*-anisidine (ex-petroleum ether)	104°	10·5	10·6
15.	Picrate of β-diethylaminopropionyl -*p*-anisidine (ex-methyl alcohol)	123°	14·82	14·9

The substances described in Table II were tested for their local anaesthetic efficiency on rabbits' cornea. Each substance was used in 2% solution and was compared with cocaine hydrochloride solution of the same strength. These results are the averages of ten experiments with each drug.

TABLE II.

(Values for coraine hydrochloride are in parenthesis)

		Time for onset of anaesthesia, complete loss of reflex action.		Duration for which complete loss of reflex action lasted.	
1.	Hydrochloride of ω-piperidinoacetyl-o-phenetidine	1 min.	(1)	28 min.	(37)
2.	Hydrochloride of diethylaminoacetyl-o-phenetidine.	1	(1½)	18 ,,	(36)
3.	Hydrochloride of β-piperidinopropionyl-o-phenetidine	5	(1)	Partial anaesthesia lasting for 19 min. (36)	
4.	Hydrochloride of β-diethylaminopropionyl-o-phenetidine	1	(1)	Partial anaesthesia lasting for 16 mins (36)	
5.	Hydrochloride of ω-piperidinoacetyl-m-phenetidine	1	(1)	48 min.	(35)
6.	Hydrochloride of diethylaminoacetyl-m-phenetidine	1	(1½)	37 ,,	(36)
7.	Hydrochloride of β-piperidinopropionyl m-phenetidine	1	(1)	Incomplete anaesthesia lasting for 30 min. (36)	
8.	Hydrochloride of β-diethylaminopropionyl-m-phenetidine	1	(1½)	Incomplete anaesthesia lasting for 25 min. (36)	
9.	Hydrochloride of ω-piperidinoacetyl-p-phenetidine	1	(1)	28 min.	(36)
10.	Hydrochloride of ω-diethylaminoacetyl-p-phenetidine	1	(1)	20 ,,	(35)
11.	Hydrochloride of β-piperidinopropionyl-p-phenetidine	1	(1)	Incomplete anaesthesia lasting for 13 min. (36)	
12.	Hydrochloride of β-diethylaminopropionyl-p-phenetidine	Never complete	(1)	Incomplete anaesthesia (35)	
13.	Hydrochloride of ω-piperidinoacetyl-o-anisidine.	1 min.	(1½)	24 minutes (35)	
14.	Hydrochloride of diethylaminoacetyl-o-anisidine	1	(1)	15 ,,	(36)
15.	Hydrochloride of β-piperidinopropionyl-o-anisidine	Never complete	(1)	Incomplete anaesthesia (35)	

TABLE II (contd.).

		Time for onset of anaesthesia, complete loss of reflex action.	Duration for which complete loss of reflex action lasted.
16.	Hydrochloride of β-diethylaminopropionyl-o-anisidine	Never complete (1)	Never complete (37)
17.	Hydrochloride of ω-piperidinoacetyl-m-anisidine	5 min. (1½)	30 minutes (35)
18.	Hydrochloride of diethylaminoacetyl -m-anisidine	10 ,, (1)	24 ,, (35)
19.	Hydrochloride of β-piperidinopropionyl-m-anisidine	Never complete (1)	Never complete (36)
20.	Hydrochloride of β-diethylaminopropionyl-m-anisidine	Never complete (1)	Never complete (37)
21.	Hydrochloride of ω-piperidinoacetyl-p-anisidine	9 min. (1)	17 min. (36)
22.	Hydrochloride of diethylaminoacetyl-p-anisidine	Never complete (1)	Never complete (36)
23.	Hydrochloride of β-piperidinopropionyl-p-anisidine	,,	,,
24.	Hydrochloride of β-diethylaminopropionyl-p-anisidine	,, ,,	,, ,,

From the above it would seem that the substances in the *meta* series have pronounced local anaesthetic action, the maximum effect being noticed in No. 5, whilst in the phenetidine series the compound No. 9 shows quite appreciable local anaesthetic activity. In both the compounds the side-chain has the piperidinoacetyl residue.

Further work is in progress. One of us (K.N.G.) is indebted to the Lady Tata Memorial Trust for a maintenance grant.

AN INVESTIGATION ON THE SOIL AND PEAT HUMIC ACIDS. PART II. OXIDATION WITH HYDROGEN PEROXIDE, HOT ALKALI AND CHLORINE DIOXIDE SOLUTION.

By G. C. Esh and S. S. Guha-Sircar.

A humic acid from peat and another from an Assam tea soil were oxidised by various strengths of H_2O_2 both as pure acid and as the Ca salt. They were also subjected to a method of degradation similar to that used by Freudenberg in connection with lignin. Products of the same nature were isolated. The acids were also oxidised by ClO_2 and oxalic and butyric acids detected in the products.

König (*Landow. jahrb.*, 1920, **55**, 185), Robinson (*J. Agric Res.*, 1927, **34**, 339), Springer (*Z. Pflanz. Dung. Bod.*, 1928, **A11** 313), Waksman (*Soil Sci.*, 1930, **30**, 97) and others have treated soils with varying concentrations of hydrogen peroxide to determine the humus content as they believed that the organic portion of the soil was more or less completely oxidised by this reagent to carbon dioxide and water. König found besides carbon dioxide, acetic and formic acids in the solution. Wheeler (*J. Soc. Chem. Ind.*, 1927, **5**, 849) also concluded that certain aliphatic carboxylic acids, especially oxalic and succinic, as well as aromatic polycarboxy acids may be formed during this reaction. Attempts have been made in the present investigation to ascertain the nature of the intermediary substances, if any, formed in the oxidation of humic acid by hydrogen peroxide.

EXPERIMENTAL.

About o·5 g. of commercial peat humic acid was dissolved in 20 c. c. of 3% caustic soda solution and hydrogen peroxide solution (50 c. c., 15%) was added at the ordinary temperature dropwise from a dropping funnel with constant stirring. Vigorous frothing accompanied the reaction. The reaction was allowed to proceed overnight. Next day the excess of hydrogen peroxide was decomposed by heating on the water-bath. The solution was then made just acid by means of hydrochloric acid and the precipitate filtered off. This precipitate was washed and analysed after conversion into barium salt. The filtrate was extracted with ethyl acetate thrice and the solvent evaporated. The acid mother-liquor left after removal of acetic acid in *vacuo* over caustic potash, was converted into a barium salt from which barium was estimated. The ethyl acetate extract on evaporation in *vacuo* gave a brownish red, gummy substance. It had a perceptible characteristic odour, like that of pyruvic acid. It gave

an instantaneous frothing in contact with a solution of sodium bicarbonate and with ferric chloride gave a violet colouration indicating its phenolic character. It also reduced an ammoniacal silver nitrate solution when heated. It also formed well defined insoluble salts of copper, lead and silver. Barium and calcium salts were formed only when the solutions were heated and kept for some time.

Attempts were made to fractionate the ethyl acetate extract. The substance is insoluble in benzene, but the major part dissolves in ether, giving a brownish solution and leaving a greyish white powdery substance. The ether-soluble portion was found to be more acidic. The two portions were separately analysed for carbon, nitrogen etc. The ether-soluble portion gave all the tests previously described more prominently. No nitrogen was found in this portion (Found: C, 44·58; H, 5·6 per cent). The substance was found to be extremely hygroscopic. The ether-insoluble portion was of a greyish white colour and was not so hygroscopic as the soluble fraction. This also gave all the previous tests. The amount was too small for analysis. The exact nature of these acids could not be cleared up. Moreover, a trace of a gummy brown substance associated with the acid could not be successfully removed. That they were phenolic or aldehydic carboxylic acids was indicated by their properties. The first fraction that separated out after treating the oxidised solution with hydrochloric acid was dissolved in ammonia and sufficient barium chloride added. The precipitated barium salt was filtered, completely washed, dried at 105° and analysed for barium. The ethyl acetate extract and the mother-liquor were analysed in the same way.

In other experiments, hydrogen peroxide of different amounts were used. In one case, the oxidised humic acid was re-oxidised with the same agent to see whether a further degradation was possible. The Ba salts in the various fractions were found to contain varied amount of barium in different preparations. Even a dilute solution of hydrogen peroxide can oxidise the humic acid molecule, but the degree of oxidation varies with the concentration of hydrogen peroxide used, the temperature, the amount of alkali present and the time given for the reaction. The optimum temperature was found to be 30-40°, the concentration of hydrogen peroxide to be 12-15% and that of the alkali 2-3%. With the increase in the amount of hydrogen peroxide added, the equivalent weight of the resulting products decreased as is seen from the increasing percentage of barium in their barium salts (vide Table I). It has been reported that the oxidation of humus is facilitated in the presence of lime. To test this view the following experiment was carried out.

Oxidation of the Ca salt of the Humic Acid by Hydrogen Peroxide.

Humic acid (10 g.) was dissolved in ammonia and sufficient calcium chloride solution added. The calcium humate formed was filtered off after complete washing with water, suspended in water without drying, and hydrogen peroxide was added very slowly drop by drop. The reaction was very slow at the ordinary temperature. The temperature of the mixture was gradually raised to 75°. It was found that the most convenient temperature was 70-80°. After complete reaction, *i.e.* when the effervescence ceased, the original calcium humate changed to a greyish white powder and this was separated from the greenish yellow filtrate by filtration and washing. The filtrate was found to be acidic. The acid filtrate on treatment with ethyl acetate gave no appreciable extract.

The white powdery mass left after oxidation of the grey calcium humate was dissolved in hydrochloric acid and the clear yellowish solution after filtration was extracted with ethyl acetate and the extract on evaporation gave a greyish white powder. This was sparingly soluble in water but dissolved in ammonia and gave a strong effervescence with a solution of sodium bicarbonate indicating its acid nature. It gave no appreciable colouration with ferric chloride. It was suspected that the acid residue was a mixture. When heated in a platinum foil a very small amount of ash was left. The ethyl acetate fraction on analysis gave C, 56·20 ; H, 6·4 per cent.

TABLE I.

Oxidation of calcium humate by H_2O_2.

Ca salt.	15% H_2O_2.	Ca in the oxidised salt.	Equiv. calc. from % Ca.
5 g.	75 c.c.	15·57%	109·45
1	20	17·35	96·25
2	50	17·79	93·45
1	30	22·62	69·9

TABLE II.

Equivalent wts. from the barium salts in the several extracts.

Humic acid.	3% KOH soln.	15% H_2O_2.	Ethyl acetate extract.	1st acid ppt.	Mother-liquor after ethyl acetate extraction.
5 g.	80 c.c.	120 c.c.	116	116	103
1	40	30	116	104	96
3	60	120	115	102	95
0·5	20	50	114	100	93

The soil humic acid was treated with hydrogen peroxide in the same way. The ethyl acetate extract in this case also showed similar phenolic and acidic properties.

Potash-fusion followed by Methylation and Permanganate Oxidation.— By mild fusion with caustic potash followed by alkaline permanganate oxidation of lignin, Freudenberg and others (*Ber.*, 1937, **70**, 500) have isolated veratric, veratroylformic and *iso*hemipinic acids and thus gave an insight into the molecular structure of lignin. The aromatic character of lignin has been amply verified. To test the correctness of this lignin hypothesis of the origin of humic acid, the following treatment was carried out. The products identical with those obtained by Freudenberg from lignin have been isolated.

Humic acid (10 g.) was suspended in water (40 c.c.) and caustic potash (90 g.) was added and the mixture was refluxed at 170°. In ½ hour the frothing started. All this time the flask was vigorously shaken. After 1½ hours the mixture was cooled to 130° and poured into 200 c.c. of water resulting in a dark brown solution. When the temperature came down to 60-70°, 140 c.c. of dimethyl sulphate was added drop by drop and the mixture kept vigorously agitated till it became acid to congo red. The methylated product that separated out, was filtered, washed with hot water thrice and dried at 100°. The filtrate was subjected to steam distillation, but no volatile organic acid was precisely detected in the distillate. The yield of the methylated product was about 8·5 g. This treatment with alkali and methylation by dimethyl sulphate was repeated till the methylation was supposed to be complete. The methylated acid was dissolved in acetone and poured into a litre of water at the room temperature, when a fine brown precipitate was thrown down, through which air was passed at 95° to remove acetone. This process gave the methylated acid in a fine state of division. It was then cooled to 60° and the liquid was treated with finely powdered potassium permanganate in portions of 3 g. with vigorous stirring. The temperature was gradually allowed to rise on a water-bath to 95° and potassium permanganate was added. After 4-5 additions the solution was cooled, nearly neutralised with 3N-sulphuric acid. The temperature was again raised to 95° and about 40 g. of more potassium permanganate were added in portions of 3 g. in the course of ½ hour. The manganese dioxide was filtered off and washed with water, and dissolved in sulphurous acid. After filtering off a small black residue the filtrate was extracted thrice with ether.

The slightly yellow alkaline filtrate from manganese dioxide was

just acidified to litmus with $2N$-sulphuric acid and extracted with ether. The ethereal solution was dried with sodium sulphate and evaporated. The residue left was a brownish gum and smelt like the lower fatty acids. This substance was fractionated further (X). The solution left after ether extraction was acidified to congo red, saturated with ammonium sulphate and then extracted with ethyl acetate Fine colourless needles separated out when the ethyl acetate extract was concentrated to a small bulk and cooled to 0°. The colourless crystals (A) separated on centrifuging and the extract was allowed to evaporate. The yellow-brown residue left was treated with hot benzene. This on cooling gave a white powder (B) which was separated by centrifuging and the cooled benzene solution on evaporation, left a gummy substance. The residue that was insoluble in hot benzene was dissolved in acetone and a slight fine white precipitate that appeared was separated by centrifuging (C). The mother-liquor after concentrating to a smaller bulk was treated with a few drops of acetonitrile and centrifuged when a white gummy substance separated out (D).

Treatment of the Ether Extract(X).—The residue left after evaporating the ethereal solution was treated with hot benzene. The benzene extract on evaporation gave a greyish waxy substance with a peculiar odour which was insoluble in water. This was neglected. The residue insoluble in hot benzene was dissolved in acetone, concentrated to a small bulk and treated with a few drops of acetonitrile, when fine colourless crystals appeared, which were separated by a centrifuge, and were dried in a vacuum desiccator. It is insoluble in water and when heated in a sealed tube it partly sublimes and partly decomposes at 250° characterist c of *iso*hemipinic acid (m.p. 249°).

Treatment of Fraction "A" of the Ethyl Acetate Extract.—The needle-like crystals separating from the cold concentrated ethyl acetate extract were again dissolved in hot benzene. The benzene solution on concentration gave fine white crystals. These crystals were insoluble in cold water but dissolved in sufficient hot water. On cooling fine crystals appeared which were centrifuged and dried in a vacuum deciccator, m.p. 178° (mixed m.p. with an authentic specimen of veratric acid).

Treatment of the Fraction (B).—The white crystals from (B) obtained on cooling the hot benzene solution of the ethyl acetate extract were separated by a centrifuge. On recrystallisation from water white crystals of veratric acid came out. The mother-liquor on treatment with charcoal and concentration gave a light yellow substance, m.p. 143°. This is possibly a mixture of veratric and veratroylformic acid.

Treatment of the Fractions (C) *and* (D).—The white gummy subs-

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tance obtained after centrifuging the acetone extract was dried in a vacuum desiccator. It was acidic and probably the high molecular acid described by Freudenberg. The clear reddish brown acetone mixture was treated with freshly heated animal charcoal whereby the red colour slightly diminished. The solution after centrifuging was treated with a few drops of acetonitrile, when a gum-like white substance separated. This was acidic and might be impure *iso*hemipinic acid.

Oxidation of the Soil Humic Acid.—The process of potash-fusion, methylation and oxidation was repeated in case of soil humic acid also, but some difference was marked in this case. The alkaline solution after oxidation was found more yellowish. When this solution was acidified with $2N$-sulphuric acid to congo red, a white amorphous mass separated out. This white mass (A) was filtered off. The acidified filtrate was first treated with ether. The ether extract (B) was faintly yellow. This acidified mother liquor was then extracted with ethyl acetate thrice.

Treatment of the portion (B).—The ether-extract was evaporated whereby a yellowish residue was obtained mixed with some white crystals. This was first extracted with hot benzene. The ether-extract was much greater in quantity than that in the case of peat humic acid. The benzene extract on evaporation gave a yellowish white residue which was dissolved in cold water. The clear greenish filtrate on slow evaporation in a vacuum desiccator gave a gummy substance which was soluble in water and on drying melted at 139°. This may be veratroylformic acid. The portion which was insoluble in cold water was dissolved in hot water and the hot solution on cooling gave white crystals of veratric acid (m.p. 178°), more of which was obtained on concentration of the mother-liquor in vacuum. The last fraction from the evaporated solution melted at 143°.

Treatment of the portion (C).—The ethyl acetate fraction when evaporated gave a reddish brown residue. Unlike the former case hot benzene could extract nothing from the residue. The acetone extract of the residue gave a gummy substance on concentration and precipitation with acetonitrile as before.

Treatment of the portion (A).—The white amorphous mass obtained after acidifying the alkaline filtrate to congo red from the oxidised humic acid was washed with water. This was also insoluble in benzene and ether but soluble in acetone. The acetone extract on evaporation gave a yellowish amorphous mass which was treated with sufficient hot water. The hot solution on cooling gave a white powdery substance which was washed with water and dried in a desiccator. This substance when heated in a sealed tube decomposed at 105° and was strongly acidic in nature.

Oxidation of Soil and Peat Humic Acids by Chlorine Dioxide Solution of different Concentrations.—Different lots of humic acids were treated with chlorine dioxide solution of different concentrations for different intervals of time. The best result was found when for 1 g. of the acid 25 c. c. of 3% chlorine dioxide solution were used and the mixture kept for 24 hours at the room temperature in the dark, 5 g of humic acids being taken in each operation. After keeping the humic acid in chlorine dioxide solution for 24 hours the insoluble portion was filtered off, washed thoroughly and then dried at 80°. The colour of the residue was light brown. Any increase either in the concentration of the solution or in the time disrupts the acid more vigorously. The filtrate was examined in the following manner :—

(*a*) A portion was evaporated to dryness. The dry contents were then extracted with ether, ethyl acetate and water successively. All the extracts were strongly acidic. The amount of water extract was greatest of all. After neutralisation with ammonia calcium chloride solution was added and the insoluble white calcium salt was treated with dilute sulphuric acid, warmed and treated with permanganate solution. The colour rapidly disappeared indicating the presence of oxalic acid.

(*b*) Another portion of the filtrate was subjected to steam distillation. A peculiar odour like that of butyric acid came out from the distillate.

(*i*) About 5 c. c. of the distillate were mixed with hydrogen peroxide solution (5 c. c.) and ferrous ammonium sulphate solution (1 c.c., 5 g. of ferrous ammonium sulphate and 10 c. c. of 40% sulphuric acid solution.). The mixture was heated at 70° for 5 minutes, treated with 6 to 7 drops of sodium hydroxide solution, cooled and filtered and 5 c. c. of the filtrate were mixed with 3 drops of alkali solution and 3 drops of 5% sodium nitroprusside solution and a slight excess of acetic acid. A red colouration developed showing the presence of butyric acid in the distillate.

(*ii*) A portion of the steam-distillate was treated with a solution containing cupric chloride bihydrate in *N*-hydrochloric acid and shaken with chloroform. On standing a slight red colour developed in the chloroform layer.

The above tests were confirmed by a blank experiment with fresh and very dilute butyric acid solution.

ESTIMATION OF CAROTENE IN GREEN VEGETABLES BY THE HILGER-SECTOR PHOTOMETER.

By BHUPAL CHANDRA RAI-SIRCAR.
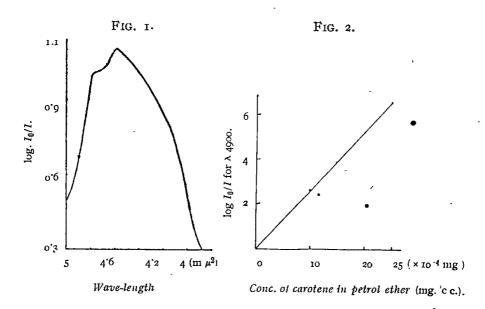
Carotene content of some thirteen varieties of green vegetables has been determined by the sector-photometric method. Pure β-carotene was taken as the standard. The extraction was done according to a method more or less similar to the procedure followed by Smith, by Schertz and by Wilson, Das-Gupta and Ahmad.

Various methods of colorimetrically estimating carotene in organic solvents are in use. Pyke (*J. Soc. Chem. Ind.*, 1936, **55**, 139T) has matched the colour in the Loviband tintometer. Guilbert (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 452) has matched the yellow colour against the the colour of a mixture of naphthol yellow and orange-G. Attempts have been made to match the colour with solutions of bixin or with solutions of inorganic salts. All these methods, however, suffer from one great drawback, the range of accurate comparison being limited within a comparatively narrow limit of concentration. There is also the additional difficulty of the matching of the exact shade of colour when different comparison standards are used. Most of the above mentioned disadvantages are absent from the spectroscopic method which was employed by Gillam (*Biochem. J.*, 1935, **29**, 1831) and De (*Indian J. Med. Res.*, 1935, **23**, 505).

The sector-photometric method was, therefore, adopted for the determination of carotene. Light from a condensed spark between two chromium electrodes (in preference to tungsten-steel electrodes as they furnish more lines in the region 4800-5000Å) passes through the solvent and the solution of a suitable concentration contained in two tubes of the same length. The emergent beam from the solvent is made to vary in intensity by varying the aperture of the rotating sector, whereas the light after absorption in the material under test passes through another rotating sector of a fixed aperture. A series of photographs is taken on a single photographic plate with the variable sector set to different apertures. Each of these photographs consists of a pair of spectrum photographs in close juxtaposition, one of which is of reduced density throughout its whole length, the other (which passed through the material) being more dense than the first in certain parts and less so in others, there being certain wave-lengths where the densities of the two are equal. The places of equal density being spotted, the absorption curve for a particular concentration of the substance in that solution is obtained. One such curve is given in Fig. 1. For

avoiding any deterioration of carotene in petroleum ether by ultraviolet rays, a solution of quinine sulphate was used as a filter and placed immediately after the source.

For measuring an unknown concentration from its absorption curve, the following procedure was adopted.

The absorption curves for a number of suitable concentrations ('0015 mg., 0'0020 mg., 0'0025 mg., per c. c.) have been obtained. The intensity of absorption for any wave-length, viz., 4900Å is measured instead of measuring the maximum absorption at 4800Å and 4600Å. The advantage of this method is that it avoids the finding out of the actual concentrations for which the maximum absorption is predominant. Next step is to plot another curve-the intensity of absorption or in other words $\log I_0/I$ (the density readings on the variable sector) for 4900Å along the ordinate and the corresponding concentration along the abscissa, a straight line passing through the origin is obtained. This is called the standard curve (Fig. 2). For measuring an unknown concentration from a knowledge of its absorption at 4900Å, the corresponding reading for the concentration is read from the standard curve.

FIG. 1.   FIG. 2.

Wave-length   Conc. of carotene in petrol ether (mg. c c.).

EXPERIMENTAL.

Methods of Complete Isolation and Purification of Carotene.—The washed green materials were cut into thin slices and dried on trays according

to the method of Schertz (*Ind. Eng. Chem.*, 1938, **30**, 1073) at 45-50°. As soon as the leaves became dry enough to crumble easily, they were ground and sieved through a 60 mesh screen of non-corrosive metal containing no copper. The powder was immediately used for extraction.

The powder (2-5 g.) was steeped in 200 c.c. of petroleum ether (b.p. 40°-70°) for 24 hours, according to Smith (*J. Biol. Chem.*, 1932, **96**, 35). The extract was filtered under reduced pressure and the residue was washed several times with petroleum ether until the washings were colourless.

The residue was again washed repeatedly with 85% acetone (Holmes and Leicester, *J. Amer. Chem. Soc.*, 1932, **54**, 716) until the extracts became completely colourless. The combined extracts containing carotene, xanthophyll and chlorophyll were transferred to a separating funnel. Acetone was washed away by shaking repeatedly with distilled water. The ethereal solution was saponified with 29% alcoholic potash according to the method of Willstätter and Mieg (*Ann. Chem.*, 1907, **12**, 355) modified by Smith (*loc. cit.*). The contents were kept for 12 hours with occasional stirring. Chlorophyllines were removed by washing with water. In case the solution is not perfectly free from green colouration, saponification was repeated (Wilson, Das-Gupta and Ahmad, *Indian J. Med. Res.*, 1937, **24**, 807). Carotene was isolated from xanthophyll by shaking with 85% methyl alcohol in accordance with the method of Willstätter and Stoll modified by Schertz (*loc. cit.*). The petroleum ether solution was dried over anhydrous sodium sulphate and concentrated to a reduced volume by distillation in vacuum. The solution was now ready for spectroscopic examination after suitable dilution. In case immediate examination was not possible, traces of extra pure hydroquinone were added to the solution and kept in an airtight bottle wrapped in black paper and preserved in a refrigerator.

It might be mentioned here that De (*Indian J. Med. Res.*, 1936, **23**, 937) also determined the carotene content of various vegetables and fruits using a spectrograph coupled with a sector but he followed a different procedure. He determined the extinction coefficient of carotene at 4630Å in petroleum ether or carbon disulphide before and after irradiation in a strong beam of ultraviolet light. Some of the numerical values obtained by him have been given in the accompanying table together with the values of the present author and those obtained by Ahmad and co-workers (*Indian J. Med. Res.*, 1937, **24**, 801) who followed a tintometric method; though the agreement is not exact still the discrepancies become obvious when it is considered

that carotene content depends on the nature of soil, season, climatic condition etc.

TABLE I.

Carotene content.

Vegetables.	Total carotene in (0·001 mg.) per 100 g. material		
	Rai-Sircar.	De.	Wilson and co-workers.
Halancha (*Enhydra fluctuans*)	2666		
Radish leaves (*Raphanus sativus*).	6666		7200-8600
Lal data (*Amaranthus gangeticus*).	2000	2520	
Lal sāk (*Amaranthus bhitum*)	6875		6750
Red puin (*Basella rubra*).	2100		3200-6500
Kalmi sāk (*Ipomoea reptans*)	3600		5200-5500
Pumpkin leaves (*Cucurbita Pepo*)	6250		5750-7200
Betel leaves (*Piper betel*) (very young).	700		
Do (mature).	8000	7200	12000
Lettuce (*Lactuca sativa*).	2116	2060	1500-1940
Palang sāk (*Beta vulgaris*)	2935	2630	
Cabbage (*Brassica oleracea*) (Inner white leaves).	833	900	
Do (outer green leaves).	2500	2380	
Carrot (*Daucus carota*)	2082	2000	2000-5600
Coriander (*Coriandrum sativum*).	13833	12630	
Dheki sāk (*Diplazium esculentum*).	3450		

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REACTIVITY OF CHCl·CCl₃-GROUP ATTACHED TO AN AROMATIC NUCLEUS.

By Hayawadan Vamanrao Dharwarkar and Rupchand Lilaram
Alimchandani.

α-Chloro derivatives of the condensation products of chloral with hydroxy- and methoxybenzoic acids have been prepared by an improved method and the reactivity of the α-chlorine atom towards potassium iodide, potassium cyanide, ammonia and aniline have been investigated and it is found that the methoxy group in the nucleus has an inhibiting influence on the α-chlorine atom.

Compounds containing the group $CHCl \cdot CCl_3$ have been obtained by a number of investigators in the course of their study of the condensation products of chloral with phenols and hydroxybenzoic acids (Chattaway and Calvet, *J. Chem. Soc.*, 1928, 2914 ; Shah and Alimchandani, *J. Indian Chem. Soc.*, 1929, **6**, 253; 1931, **8**, 261; Hurry and Meldrum, *ibid.*, 1934, **11**, 535). As very little work has been done so far regarding the behaviour of the $CHCl \cdot CCl_3$ group, an attempt has been made by the present authors to study the reactivity of this group in general and of the α-chlorine atom in particular.

The tetrachloro compound, $R \cdot CHCl \cdot CCl_3$, is usually derived from the chloral condensation product containing $CHOH \cdot CCl_3$ group by (a) saturating the sulphuric acid solution of the substance with dry hydrochloric acid gas (*cf.* Chattaway and Calvet, *loc. cit.*), (b) treatment with hot concentrated sulphuric acid (*cf.* Shah and Alimchandani, *loc. cit.*), and (c) the interaction of thionyl chloride or phosphorus pentachloride (*cf.* Feist, Nissen and Städler, *Ber.*, 1914, **47**, 1173; Hurry and Meldrum, *loc. cit.*). In the present investigation, however, it has been found that the yield and purity of the product can be considerably increased by producing hydrochloric acid gas *in situ* by adding sodium chloride to the sulphuric acid solution of the substance.

Employing the above method, 2-hydroxy-5-αββ-tetrachloroethylbenzoic acid (I) and 4-hydroxy-5-αβββ-tetrachloroethylbenzoic acid (II) have been prepared from salicylic and *p*-hydroxybenzoic acids respectively in addition to the corresponding methoxy compounds (III) and (IV) already obtained from methoxysalicylic acid (Hurry and Meldrum, *loc. cit.* ; Shah and Alimchandani, *J. Indian Chem. Soc.*, 1936, **13**, 476), and from anisic acid (Chattaway and Calvet, *loc. cit.*) respectively. But attempts to obtain

similar compounds from *m*-hydroxy- and *m*-methoxybenzoic acids failed owing to the formation of the phthalide ring (Fritsch, *Annalen*, 1897, 276, 344).

Each of the above tetrachloro compounds, $R \cdot CHCl \cdot CCl_3$, can be reduced to $R \cdot CH : CCl_2$ by means of zinc dust and acetic acid. These will be described in a subsequent paper.

A solution of potassium iodide in acetone or alcohol easily removes the α- and β-chlorine atom from the hydroxy compounds yielding ethylene derivatives identical with the above-mentioned reduction products (*cf.* Van Duin, *Rec. trav. Chim.*, 1926, 45, 345; Dillong and co-workers, *J. Amer. Chem. Soc.*, 1930, 52, 1953); thus (I) and (II) give 2-hydroxy-, and 4-hydroxy-5-ββ-dichlorovinylbenzoic acids respectively. The methoxy compounds (III) and (IV), however, are unaffected. The compound (I) on interaction with ammonia and aniline gives 2-hydroxy-5-α-amino-βββ-trichloroethylbenzoic acid and 2-hydroxy-5-α-anilino-βββ-trichloroethyl-benzoic acid respectively. The action of potassium cyanide is interesting. The replacement of α-chlorine atom by the CN group is accompanied by the elimination of a molecule of HCl as well during the reaction thus giving 2-hydroxy-5-α-cyano-ββ-dichlorovinylbenzoic acid (V), $R \cdot C(CN):CCl_2$.

The hydrolysis of CN group to COOH by means of concentrated hydrochloric or sulphuric acid could not be accomplished. Alkali, however, easily hydrolyses the side-chain giving 4-hydroxy-5-carboxyphenylacetic acid.

It is significant that the hydroxy compounds (I) and (II) are very unstable even towards cold dilute alkali, but no definite product could be isolated. The methoxy compounds (III) and (IV), on the other hand, are sufficiently stable to cold dilute alkali. Treatment with hot aqueous alkali, however, eliminates a molecule of hydrochloric acid furnishing 4-, and 2-methoxy-5-carboxy-1-αββ-trichlorostyrene respectively (*cf.* Shah and Alimchandani, *loc. cit.*)

Similarly it is interesting to note that (III) and (IV) do not react with potassium cyanide, potassium iodide, ammonia and aniline [contrast the behaviour of the corresponding hydroxy compounds (I) and (II).]

The authors believe that the inactivity of the α-chlorine atom of the methoxy derivatives is due to the OMe group which causes a large diminution in the ionising tendency of the α-chlorine by a supply of electrons and as a result the halogen atom becomes resistant towards anionic attack like ammonia, aniline, potassium iodide and potassium cyanide (*cf.* Baddeley and Bennet, *J. Chem. Soc.*, 1933, 265).

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EXPERIMENTAL.

2-Hydroxy-5- αββ-tetrachloroethylbenzoic Acid (I).—Chloral hydrate (40 g.) and salicylic acid (28 g.) were dissolved in concentrated sulphuric acid (200 c.c.) in a pressure bottle and sodium chloride (12 g.) was quickly added, and the bottle was kept sealed with paraffin for 2 days. The reaction mixture was then poured into ice when a pasty mass separated which solidified on washing with water. It was first crystallised from glacial acetic acid and then from carbon tetrachloride in shining rhombic plates, m.p. 182-83°, yield 25 g.' The compound decomposes in presence of alkali and gives violet colouration with ferric chloride. (Found: Cl, 46·71. $C_9H_6O_3Cl_4$ requires Cl, 46·69 per cent).

The compound was also obtained by dissolving 2-hydroxy- 5-α hydroxy-βββ-trichloroethylbenzoic acid (5 g. Calvet and Mejuto, *J. Chem. Soc.*, 1936, 554) in concentrated sulphuric acid (50 c.c.) and saturating the solution with dry hydrochloric acid gas.

The *acetyl* derivative was crystallised from chloroform in thin plates, m.p. 146-47°. (Found: Cl, 41·44. $C_{11}H_8O_4Cl_4$ requires Cl, 41·0 per cent).

The *anilide* was crystallised from chloroform in yellowish silky needles, m.p. 201-2°. (Found: Cl, 37·36. $C_{15}H_{11}O_2NCl_4$ requires Cl, 37·41 percent).

The *p-toluidide* crystallised from a mixture of chloroform and petroleum benzine in thin leaflets, m.p. 178—79°. (Found: Cl, 36·12; $C_{16}H_{13}O_2NCl_4$ requires Cl, 36·07 per cent).

2-Hydroxy-5- α-amino-βββ-trichloroethylbenzoic Acid.—The tetrachloro compound (I, 5g.) was dissolved in rectified spirit (50 c.c.) and liquor ammonia (*d* 0·9) was added till there was a distinct smell of ammonia and shaken well for 2 hours. After 5 days the excess of ammonia was removed under reduced pressure in a vacuum desiccator. The solution was diluted with about 20 c.c. of water, evaporated on a water-bath to a small bulk and acidified with dilute hydrochloric acid when a tarry oil separated. After the removal of the tar the solution slowly deposited a crystalline product which crystallised from rectified spirit in needles, m.p. 212° with previous charring at 183—84°. It dissolves in sodium hydroxide with purple colouration and gives out ammonia and carbylamine on heating the solution. (Found: Cl, 37·93; N, 4·9. $C_9H_8O_3NCl_3$ requires Cl, 37·5; N, 4·92 per cent).

2-Hydroxy-5- α-anilino- βββ-trichloroethylbenzoic Acid.—A solution of (I, 3 g.) in benzene (50 c.c.) and aniline (1·3 g.) was refluxed on a water-bath for 2 hours. The solid product obtained on cooling was crystallised

from benzene It was recrystallised from rectified spirit in lustrous rhombic plates, m.p. 182° (decomp.). (Found: Cl, 29·81. $C_{15}H_{12}O_3NCl_3$ requires Cl, 29·50 per cent).

Reduction of (I) *by Zinc dust and Acetic Acid*: 2-*Hydroxy-5-ββ-dichlorovinylbenzoic Acid.*—Zinc dust (2 g.) was added gradually to a hot solution of (I, 5 g.) in glacial acetic acid (50 c.c.). After the reaction was over the solution was quickly filtered and diluted with water when a mass of soft silky needles separated. It was filtered off and crystallised from benzene, m.p. 170°.

It does not absorb bromine in either acetic acid or chloroform solution. It decolourises permanganate and gives blue ferric reaction. (Found: C, 46·53; H, 2·73; Cl, 30·10. $C_9H_6O_3Cl_2$ requires C, 46·35; H, 2·6; Cl, 30·44 per cent).

Action of Potassium Iodide on (I). 2-*Hydroxy-5-ββ-dichlorovinylbenzoic Acid.*—Potassium iodide (3·5 g.) was added to a solution of (I, 3 g.) in acetone (50 c.c.) and refluxed on a water-bath for about 15 minutes. After removing iodine by steam distillation, needle-shaped crystals were deposited which crystallised from rectified spirit, m.p. 170-71°.

2-*Hydroxy-5- α-cyano- ββ-dichlorovinylbenzoic Acid* (V).—An aqueous solution of potassium cyanide (2 g.) was added to the solution of (I, 5 g.) in rectified spirit (30 c. c.) and refluxed for 2 hours on a water-bath. The solution was filtered and acidified with dilute hydrochloric acid when a pasty mass was obtained which was washed with water, dried on a porous plate and crystallised from a mixture of acetone and benzene in fine silky needles, m. p. 224-25°. It gives with ferric chloride a violet colouration. (Found : Cl, 27·66 ; N, 5. 45. $C_{10}H_5O_3NCl_2$ requires Cl, 27.49; N, 5.43 per cent).

The *acetyl* derivative crystallised from rectified spirit in double pyramids, m.p. 175-76°. (Found : Cl, 23·72. $C_{12}H_7O_4NCl_2$ requires Cl, 23·63 per cent).

The *dibromide* was obtained bp adding bromine to the substance dissolved in acetic acid. The product crystallised from benzene in white silky needles, m.p. 210°. (Found: Halogen, 55.72. $C_{10}H_5O_3NCl_2Br_2$ requires Halogen, 55·26 per cent).

Hydrolysis of (V) *by Alcoholic Potash :* 4-*Hydroxy-5-carboxyphenylacetic Acid.*—The compound (V. 5 g.) was refluxed with 20% alcoholic potash (25 c.c.) for 3 hours until the evolution of ammonia ceased. The solution was acidified and extracted with ether. On removing ether, a gelatinous mass was obtained which was first crystallised from acetic acid and then from chloroform in rhombic plates, m.p. 207°. (Found : C, 54.97 ;

H, 4·23 ; Equiv., 97·24. $C_9H_8O_5$ requires C, 55·09 ; H, 4·11 per cent. Equiv., 98·08).

Oxidation of (V) : *Formation of 4-Hydroxyisophthalic Acid.*—The compound (V, 1 g.) was dissolved in 5% sodium hydroxide solution making the solution just faintly alkaline. Hydrogen peroxide (12 vol., 15 c.c.) was added, and the solution shaken well for ½ hour and acidified with dilute hydrochloric acid. The product crystallised from a mixture of methyl alcohol and chloroform in needles, m.p. 303° (mixed m.p. with 4-hydroxy-*iso*phthalic acid).

4-Methoxy-5-carboxy-1-αββ-tetrachloroethylbenzene.—Chloral hydrate (10 g.) and methoxysalicylic acid (8 g.) were dissolved in concentrated sulphuric acid (80 c.c.) and treated with sodium chloride (4 g.) as mentioned before. After 5 days, the mixture was poured into ice when a pasty mass separated, which solidified on washing with water. It was crystallised from glacial acetic acid and then from rectified spirit in prismatic plates, m. p. 138°. (*cf.* Hurry and Meldrum, *loc. cit.* Shah and Alimchandani, *ibid.*, 1936, **13**, 475).

The *methyl ester* crystallised from benzene in long hexagonal plates, m.p. 105°. (Found : Cl, 42·65. $C_{11}H_{10}O_3Cl_4$ requires Cl, 42·71 per cent).

4-Methoxy-5-carboxy-1-αββ-trichlorovinylbenzene.—The above-mentioned compound (8 g.) was refluxed with 15% alcoholic potash (40 c.c.) for ½ hour. The solution was filtered, acidified and the product obtained was crystallised from rectified spirit in white silky needles, m.p. 151-52°, yield 3 g.

It does not absorb bromine in acetic acid, chloroform or carbon tetrachloride. Potassium permanganate is not decolourised in the cold. (Found : Cl, 37.69 ; Equiv., 281·1. $C_{10}H_7O_3Cl_3$ requires Cl, 37·82 per cent. Equiv., 281. 4).

The *calcium salt* crystallises with 5½ molecules of water of which 3½ molecules are lost at 110°. [Found : Ca, 5·72. $(C_{10}H_6O_3Cl_3)_2Ca,5½ H_2O$ requires Ca, 5·73 per cent].

The *methyl ester* crystallises from benzene in long needles, m.p. 85°. (Found : Cl, 35·97. $C_{11}H_9O_3Cl_3$ requires Cl, 36·03 per cent).

4-Hydroxy-5-αββ-tetrachloroethylbenzoic Acid (II).—*p*-Hydroxybenzoic acid (20 g.) and chloral hydrate (30 g.) were dissolved in sulphuric acid (200 c.c.) and mixed with sodium chloride (6 g.) as usual. After a week the mixture was poured over ice and the pasty mass obtained was dried on a porous tile and crystallised first from glacial acetic acid and then from benzene-petroleum benzine in glistening rhombic plates, m·p.·142° (efferv.). Ferric chloride produces very feeble purple colouration. (Found : Cl, 46·65. $C_9H_6O_3Cl_4$ requires Cl, 46·69 per cent).

The *acetyl derivative* crystallised from rectified spirit in rectangular rods, m.p. 189-90°. (Found : Cl, 41·32. C$_{11}$H$_8$O$_4$Cl$_4$ requires Cl, 41·0 per cent).

Action of Potassium Iodide on (II) : *4-Hydroxy-5-ββ-dichlorovinylbenzoic Acid.*—The compound (II, 1·5 g.) was dissolved in rectified spirit (10 c.c.) and refluxed with potassium iodide (9 g.) for 20 minutes. On dilution with water needle-shaped crystals were obtained which were recrystallised from benzene, m.p. 171°. (Found : Cl, 30·23. C$_9$H$_6$O$_3$Cl$_2$ requires Cl, 30·44 per cent).

2-Methoxy-5-carboxy-1-αββ-tetrachloroethylbenzene (*cf.* Chattaway and Calvet, *loc. cit*).—Anisic acid (24 g.) and chloral hydrate (30 g.) were dissolved in concentrated sulphuric acid and mixed with sodium chloride (12 g.) in the usual manner. After 3 days the mixture was poured over ice and the precipitated solid mass was first crystallised from glacial acetic acid and then from methyl alcohol in needles, m.p. 248-49°, yield 29 g.

The *methyl ester* crystallised from benzene in square plates, m.p. 110-11°. (Found : Cl, 42·83. C$_{11}$H$_{10}$O$_3$Cl$_4$ requires Cl, 42·71 per cent).

2- Methoxy- 5- carboxy-1- αββ- trichlorostyrene.—The above-mentioned compound (5 g.) was refluxed with 20% alcoholic potash (20 c.c.) for 15 minutes, the solution diluted with water and acidified. The precipitate obtained was crystallised from rectified spirit in orange cubes, m.p. 212-13°. (Found : Cl, 37·73. C$_{10}$H$_7$O$_3$Cl$_3$ requires Cl, 37·82 per cent).

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SYNTHETIC INVESTIGATIONS ON THE DEGRADATION PRODUCTS OF BILE-ACIDS, SEX HORMONES ETC. PART I. A SYNTHESIS OF 7-METHYL-0:3:3-BICYCLOOCTANE-1-ONE.

By D. K. BANERJEE.

A synthesis of 7-methyl-o:3:3-bi*cyclo*octane- 1 one by the cyclisation of ethyl 1-methyl-1-carbethoxy-*cyclo*pentane-2-β- propionate has been described. The fused carbon ring, thus formed, is found to be mainly *trans*-.

By the oxidation of desoxycholic acid Wieland and co-workers (Wie-land and Schlichting, *Z. physiol. Chem.*, 1924, **134**, 276 ; Wieland and Vocke, *ibid.*, 1928, **177**, 68) obtained a tetrabasic acid $C_{16}H_{24}O_8$. Its thermal decomposition resulted in the formation of a pyroketo-dicarboxylic ·acid $C_{15}H_{22}O_5$ (I) which is now regarded as a 7-methyl-o:3:3- bicyclo-octane-1-one derivative, on the basis of the new constitution assigned to the cholane skeleton (Wieland and Dane, *Z. physiol. Chem.*, 1933, **216**, 91)

$$HO_2C'H_8C_4 \quad Me$$

(I)   (II)

In a previous paper (Mitter and Banerjee, *Ber.*, 1936, **69**, 456) an investigation on the synthesis of the above type of compound has been described. As a preliminary to the synthesis of the pyroketo-dicarboxy ic acid (I), a method for the synthetical preparation of 7-methyl-o:3:3- bicyclo-octane-1-one (II) has been dealt with in the present communication. A preparation of a 7-methyl o:3:3 bi*cyclo*-octane-2-one has been described by Linstead and Errington (*J. Chem. Soc.*, 1938, 666) in which a rigid proof regarding the position of the keto group is wanting.

Ethyl cyanoacetate has been condensed with ethyl levulate in presence of acetamide according to the method of Cope (*J. Amer. Chem. Soc.*, 1937, **59**, 2327), and an excellent yield of ethyl 1-cyano-2-methyl−Δ^1-butene-1:4-dicarboxylate (VI) is obtained. Addition of potassium cyanide to the above unsaturated cyano-ester is carried out according to the method of Hope and Sheldon (*J. Chem. Soc.*, 1922, **121**, 2223). The resulting dicyano-

ester (V) is hydrolysed and the crude gummy acid, thus obtained, is esterified by alcoholic sulphuric acid to yield the tricarboxylic ester (IV). Condensation of cyano-acetic ester with keto-esters and subsequent addition of potassium cyanide to the resulting unsaturated cyanoesters has first been carried out by Hope (*J. Chem. Soc.*, 1912, 911, Hope and Sheldon, *loc. cit.*) and later by Bardhan and Ganguly, *ibid.*, 1936, 1852; *Science and Culture*, 1937, **2**, 655). Condensation of cyano-acetic ester with the keto group according to the method of Cope (*loc. cit.*) has, however, given more satisfactory result.

The sodio-salt of (III, $R=R'=CO_2Et$; $R''=H$) has been condensed with ethyl β-chloropropionate to yield ethyl 2:3-dicarbethoxy-3-methyl-*cyclo*pentanone-2-β-propionate [III, $R=R'=CO_2Et$; $R''=(CH_2)_2CO_2Et$], (*cf. Baker, J. Chem. Soc.*, 1931, 1552), which on hydrolysis yields the keto-acid [III, $R=H$; $R'=CO_2H$; $R''=(CH_2)_2CO_2H$]. Ethyl 1-methyl-1-carbethoxy-*cyclo*pentane-2-β-propionate (VIII, $R=CO_2Et$; $R'=CH_2\cdot CH_2 CO_2Et$), which is obtained by the reduction of the above keto-acid by Clemmensen's method followed by esterification of the gummy acid obtained therefrom, is cyclised by sodium in benzene solution to yield 7-methyl-2-carbethoxy-o:3:3-bi*cyclo*octane-1-one (VII). The yield of the above cyclisation product is only 30%. 7-Methyl-o:3:3-bi*cyclo*octane-1-one (II) is obtained by the hydrolysis of the β-ketonic ester (VII).

$$CH_3\cdot CO\cdot[CH_2]_2\cdot CO_2Et \qquad CH_3\cdot C\cdot[CH_2]_2\cdot CO_2Et \qquad CH_3\cdot C(CN)\cdot[CH_2]_2\cdot CO_2Et$$
$$+ \qquad\qquad\qquad\quad \parallel \qquad\qquad\qquad\qquad\quad |$$
$$CH_2\cdot(CN)\cdot CO_2Et \qquad\quad C(CN)\cdot CO_2Et \qquad\qquad CH(CN)\cdot CO_2Et$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad (VI) \qquad\qquad\qquad\qquad\qquad (V)$$

$$\rightarrow CH_3\cdot C(CO_2Et)\cdot[CH_2]_2\cdot CO_2Et$$
$$| \qquad\qquad\qquad \rightarrow$$
$$CH_2\cdot CO_2Et$$
$$(IV)$$

(III)

(VIII)

(VII)

To determine the locking of the fused carbon rings in (II) the ketone has been oxidised with nitric acid to 1-methyl-*cyclo*pentane-1-carboxylic-2-acetic acid (VIII, $R=CO_2H$; $R'=CH_2\cdot CO_2H$), which after two

crystallisations from water melts at 126-27°. Both the *cis*-form (m.p. 110°) and the *trans*-form (m.p. 139°) of the above acid have been synthetically prepared by Linstead and Errington (*loc. cit.*), and they have shown the *cis*-acid to be identical with the acid obtained from 7-methyl-o:3:3-bi*cyclo*octane. But the acid obtained in our case seems to be mainly the *trans*-isomeride. The low yield of (VII) also lends support to the same conclusion. A similar mixture of stereoisomerides of acid (VIII, R=CO₂H ; R'=CH₂·CO₂H) of m.p. 126° consisting mainly of the *trans*-form was obtained by Barrett, Cook and Linstead (*J. Chem. Soc.*, 1935, 1065), when they prepared the reference compound. It has, however, been pointed out at a later stage that the acid which was described as melting at 126°, was on repeated crystallisation from water found to melt at 132-133° ; the mixed melting point of the latter with the acid of m.p. 139° was 136°. For want of sufficient material, however, further crystallisation of the acid, now prepared, could not be carried out. The b.p. of 7-methyl-o:3:3-bi*cyclo*octanone obtained by Linstead and the m.p. of its semi-carbazone are 80°/12 mm. and 178° respectively, whereas the b.p. of 7-methyl-o:3:3-bi*cyclo*octane-1-one and the m.p. of its semicarbazone are 70°/6 mm. and 210° respectively.

It is interesting to note that the stabilisation of the *trans*-form in the fused *cyclo*pentano-*cyclo*pentane system due to the presence of the angular methyl group (which according to Hückel should exhibit a moderate degree of strain) is also exhibited by the pyroketo-dicarboxylic acid (I) which, as has already been mentioned, is formed by the thermal decomposition of the acid C₁₆H₂₄O₈. Wieland has proved the stereoisomeric constitution of (I) by showing its oxidation product to be identical with the *trans*-form of the C₁₃H₂₀O₆ acid, the *cis*-form of which was prepared by the same worker by conversion of the *trans*-acid to the *cis*-anhydride followed by treating the anhydride with warm water.

E X P E R I M E N T A L.

Ethyl 1-cyano-2-methyl- Δ^1 *-butene-1:4-dicarboxylate* (VI).—A mixture of ethyl levulate (53·5 g), ethyl cyanoacetate (40 g.), acetamide (8 g.) and glacial acetic acid (85 c.c.) was slowly distilled from a Claisen's flask provided with a fractionating column, the temperature of the distilling vapours being kept between 105-115°. In course of about 7 hours, 86 c.c. of the distillate were collected. The residue in the flask was taken up in ether and washed several times with water. After the removal of the ether the product was fractionated. Almost the whole of the unreacted keto-ester and cyanoacetic ester, which were collected in the lower boiling

fraction, were used in subsequent lots. The unsaturated cyano-ester (55 g.) distilled at 154-160°/5·5 mm. (Found. N, 5·6. $C_{12}H_{17}O_4N$ requires N,5·85 per cent).

Diethyl 1:2-dicyano- 2-methyladipate (V).—Potassium cyanide (17 5 g.) dissolved in water (95 c.c.) was slowly added with constant shaking to a solution of ethyl 1-cyano-2-methyl-$\triangle^1$-butene-1:4—dicarboxylate (32 g.) in alcohol (152 c.c.) and water (8 c.c.). The above mixture was cooled in ice and with shaking a cooled solution of hydrochloric acid (21·3 c.c. d1·15) and water (15 c.c.) (equivalent to three-fourth of the quantity of potassium cyanide added), were slowly added. The resulting slightly opaque solution was left at the room temperature for about 20-25 minutes and then acidified by pouring into a large volume of a very dilute hydrochloric acid, when a heavy oil separated. The oil was extracted. with ether, the ethereal solution washed with water and dried over sodium sulphate, ether removed and diethyl 1:2-dicyano-2-methyl-adipate collected at 190-192°/6· mm., yield 80-90%. (Found: N, 10·6. $C_{13}H_{18}O_4N_2$ requires N, 10·5 per cent).

Diethyl 2-Methyl-2-carbethoxyadipate (IV).—The above dicyano-ester (60 g.) was hydrolysed by refluxing with 8 times its volume of concentrated hydrochloric acid for 12 hours. The resulting clear solution after saturation with common salt, was repeatedly extracted with ether. The ethereal solution was dried over freshly ignited sodium sulphate and the crude gummy acid (29 g.), obtained after the removal of ether, was esterified by refluxing with a solution of alcoholic sulphuric acid (300 c.c. absolute alcohol and 50 c.c. sulphuric acid, d 1·84), for 36 hours on a water-bath. The ester was isolated in the usual manner and distilled at 169-170°/10 mm., yield 31 g. (Found : C, 58·5; H, 8·1. $C_{14}H_{24}O_6$ requires C, 58·3; H, 8·3 per cent).

Ethyl 3-Methyl-cyclopentanone-2 : 3-dicaiboxylate (III).—The tricarboxylic ester (IV) in sodium-dried benzene (100 c.c.) was refluxed with powdered sodium (4·6 g) on the water-bath for 3-4 hours until all the sodium went into solution. The cooled benzene solution was acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated after dilution with ether, washed with sodium bicarbonate solution and then with water. The mixture of benzene and ether was removed. The residual oil, which gave a deep violet colouration with alcoholic ferric chloride, boiled at 153°/8·5 mm., yield 22 g. (Found: C, 59·3 ; H, 7·1. $C_{12}H_{18}O_5$ requires C, 59·5 ; H, 7·4 per cent).

Ethyl 2 : 3-Dicarbethoxy-3-methyl-cyclopentanone-2-β-propionate [III, R = R′ = CO_2Et, R″ = $(CH_2)_2CO_2$ Et).—To the sodio derivative of the

above β-ketonic ester, prepared by allowing a mixture of pulverised sodium (2·9 g.) suspended in dry benzene (100 c.c.) and 2 : 3-dicarbethoxy-3-methyl-*cyclo*pentanone (30 g.) to stand overnight, ethyl β-chloropropionate (18 g.) was added and the whole was refluxed on a water-bath for 24 hours. Water was added to the cooled reaction mixture, the benzene layer separated, washed with water and dried. The solvent was .removed and the residue distilled at 194-97°/7 mm., yield 31 g. The ketonic ester does not respond to ferric chloride reaction. (Found : C, 59·2 ; H, 7·5. $C_{17}H_{28}O_7$ requires C, 59·6 ; H, 7·6 per cent). The potassium salt of the β-ketonic ester on condensation with ethyl β-chloropropionate in xylene solution, yielded the condensation product in poor yield.

3-C*arboxy-3-methyl*-cyclo*pentanone-2-β-propionic Acid* [III, R=H ; $R' = CO_2H$; $R'' = (CH_2)_2 CO_2H$).]—The above ester (13·5 g.) was hydrolysed by boiling with concentrated hydrochloric acid (50 c.c.) for 36 hours. The acid solution was extracted with ether and the oily residue left after the removal of ether solidified on being kept in a vacuum desiccator. On crystallisation from ether it separated in prismatic needles, m.p. 116°, yield 8-9 g. (Found : C, 55·6 ; H, 6·6 ; Equiv., 105·3. $C_{10}H_{14}O_5$ requires C. 56·07 ; H, 6·5 per cent. Equiv., 107).

The *semicarbazone* of the above keto-acid, on crystallisation from dilute alcohol, melted at 228°. (Found : N, 15·6. $C_{11}H_{17}O_5N_3$ requires N 13·6 per cent).

Ethyl 1-*Methyl* -1-*carbethoxy*cyclo*pentane-2-β-propionate* (VIII, R= CO_2Et ; $R' = CH_2 \cdot CH_2 \cdot CO_2Et$).—A mixture of amalgamated zinc (50 g.), the above keto-acid (18 g.) and concentrated hydrochloric acid (d 1·1ε, 200 c.c.) was refluxed for 12 hours, 100 c.c. more of concentrated hydrochloric acid were then added and the heating under reflux continued for another 12 hours. After cooling, the acid solution was repeatedly extracted with ether. On removal of the solvent, a syrupy liquid was left as a residue which, however, showed no tendency to crystallise. The crude liquid acid (about 10 g.) was dried in a vacuum desiccator and esterified by refluxing with absolute alcohol (50 c.c.) and concentrated sulphuric acid (d 1·84, 5 c.c.) for 24 hours. The dibasic ester on being worked up in the usual manner boiled at 140-142°/4·5-5 mm., yield about 10 g. (Found : C, 65·2 ; H, 9·1. $C_{14}H_{24}O_4$ requires C, 65·6 ; H, 9·4 per cent).

7-*Methyl-2-carbethoxy*-o : 3 : 3-*bicyclooctane-1-one* (VII).—The above dicarboxylic ester (10 g.) was refluxed with sodium dust (1·8 g.), suspended in dry benzene (25 c.c.), for 5 hours. The reaction mixture was cooled and treated with ice-cold dilute hydrochloric acid. The benzene

layer was separated and treated 'in the usual manner. On removal of benzene 7-methyl-2-carbethoxy-o : 3 : 3-bicyclooctane-1-one (2'5 g.) distilled at 119-120°/6 mm., leaving some undistillable residue in the flask. The above ester gives a characteristic violet colouration with alcoholic ferric chloride. (Found : C, 69'2 ; H, 8'5. $C_{12}H_{18}O_3$ requires C, 68'6 ; H, 8'6 per cent).

7-*Methyl*-o : 3 : 3-*bicyclooctane*-1-*one* (II).—The keto-ester (VII, 2'4 g.) was hydrolysed by refluxing for 16 hours with an excess of 20% sulphuric acid. The resulting product was taken up in ether, the ethereal layer was washed with sodium carbonate solution and then with water, dried and the ether removed. On distillation 7-methyl-o : 3 : 3-bicyclooctane-1-one was obtained as a colourless oil with strong camphoraceous smell, b.p. 70°/6 mm. (Found: C, 77'7 ; H, 10'06. $C_9H_{14}O$ requires C, 78'2 ; H, 10'1 per cent). The *semicarbazone* crystallised from ethyl alcohol, m.p. 210°. (Found: N, 21'7. $C_{10}H_{17}ON_3$ requires N, 21'5 per cent).

Oxidation of 7-*Methyl*-o : 3 : 3-*bicyclooctane*-1-*one*.—The ketone (II) (0'7 g.) was heated on the water-bath with concentrated nitric acid (4 c.c.) for 2 hours and then on the free flame for 7 hours with the addition of 4 c.c. of water. The clear solution was concentrated by keeping it in a vacuum desiccator over caustic potash when crystals of the dibasic acid separated, m.p. 123° with previous, shrinking at 120°. After two crystallisations from water it had m.p. 126-27°. (Found : C, 58'06 ; H, 7'53. $C_9H_{14}O_4$ requires C, 58'07 ; H, 7'53 per cent).

My thanks are due to Prof. P. C. Mitter for valuable advice and encouragement during the course of this work. My thanks are also due to Mr. N. Ghosh and Mr. B. Bhattacharyya for carrying out the microanalysis of some of the compounds.

PHOTOCHEMICAL AFTER-EFFECT IN THE OXALATE-IODINE REACTION

BY P. S. MacMAHON AND BIJAN BIHARI LAL.

The after-effect rate in the oxalate-iodine reaction increases with the length of period of pre-illumination. The shapes of the curves obtained indicate that the after-effect rate of reaction is identical with the photochemical rate at the instant of darkening. It falls off very rapidly at first, so that it has already been largely reduced by the time the first reading is taken. The duration of the after-effect, *i.e.*, period during which a measurable falling velocity can be detected by the disappearance of I_2, is independent of temperature and period of pre-illumination. The end-rates, when the fall in velocity becomes very slow, are found to be at a higher level than the normal dark reaction to an extent depending upon the period of pre-illumination. The value of the "secondary after-effect" obtained by adding fresh iodine in the dark to solutions in which all the original iodine has been used up by exposure to light is diminished (a) with increase of the time interval between decolourisation and addition of iodine, (b) with increase of temperature and (c) with increase of concentration of KI. In the absence of iodine the "activity" disappears completely in the course of time depending upon the temperature.

Solutions of free oxalic acid and iodine react photochemically but there is no after-effect. Mixtures of oxalate (or oxalic acid) and iodine from which all the molecular iodine has been removed photochemically do not reduce mercuric chloride, indicating the absence of "activated oxalic acid" in the sense in which the term has been applied in the permanganate-oxalate reaction. A mechanism has been suggested dispensing with assumptions about the existence of activated molecules, and depending solely upon a simple extension of the Berthoud chain mechanism for the oxalate-iodine photo-reaction.

The object of this investigation was to try and examine, if only from a phenomenal point of view, whether there is any relation between the after-effect in the potassium oxalate-iodine reaction, and the so-called "activation" of oxalic acid by the addition of small quantities of potassium permanganate to it in aqueous solution. It is only natural to suppose that these two reactions may have a common origin, namely, that light energy absorbed in the first instance, or chemical energy liberated by the primary act of oxidation in the second, may be transferred to oxalic acid molecules or ions, conferring upon them the enhanced reactivity shown, for example, in their behaviour with mercuric chloride in the latter instance.

The apparent close parallelism between the two has been further emphasised by the observations of Abel (*Z. Elektrochem.*, 1937, **43**, 629) that a mixture of potassium oxalate and iodine after having been de-colourised by illumination shows enhanced reactivity towards iodine subsequently added in the dark, over and above the normal dark rate. The question arises whether such end solutions may not also contain some form of activated product identical with or similar to that produced in

the permanganate-oxalic acid reaction. The latter will be the subject of a further communication.

The following account shows the results which have been obtained from a more detailed study of the after-effect in potassium oxalate-iodine-potassium iodide mixtures under varying degrees of concentration and temperature.

Effect of Time of Illumination.

There is a measurable dark reaction between potassium oxalate and iodine which has been found by previous workers to be unimolecular with respect to iodine. On illumination of solutions with the light of a 500-watt filament lamp for a short time, we find that a marked after-effect is produced, the initial rate of which increases continuously with the time of pre-illumination.

Table I shows the course of an experiment in detail. First readings for the after-effect were taken as soon as practicable after darkening. In all cases, the corresponding dark rate has been subtracted from the total effect to give the after-effect rate. For the calculation of the velocity constants for the after-effect, zero time has been reckoned from the moment the first reading was taken after cutting off the illumination. The pre-illuminated reaction mixtures were always shaken before taking the first observation in the dark.

TABLE I.

Temperature of thermostat $= 50°$. Concentrations: $N/2\text{-}K_2C_2O_4$, $N/30\text{-}$ KI, $N/120\text{-}I_2$.

$K = 1/t \log a/a\text{-}x$, where a is the initial concentration of iodine and $a\text{-}x$ is the concentration at time t.

A. Dark reaction.			B. Illuminated at the point marked.*		
Time.	$Na_2S_2O_3$	$K \times 10^6$.	Time.	$Na_2S_2O_3$	$K \times 10^6$
0 min.	8·10 c.c.	—	0 min.	8·00 c.c.	—
66	7·45	550	68	7·35	541
120	6·90	581	120	6·90	536
180	6·40	568	180	6·30	576
245	5 95	547	190*—205 i e., 15 min.		illumination
300	5·45	574			$K \times 10^6$.
435	4·65	554	205	4·05	—
540	4·00	567	225	3·35	413
			250	3·20	228
			308	2·80	156
			441	1·90	139
			540	1·40	138
			685	0·95	131

Table II shows the effect of time of illumination at 50°. The initial concentrations of the reactants were the same as in Table I.

TABLE II.

Time of illumination.

15 min.		10 min.		5 min.		1 min	
	After-effect						
t.	$K \times 10^5$.	t.	$K \times 10^5$.	t.	$K \times 10^5$.	t.	$K \times 10^5$.
o min.	...	o min.	...	o min.	...	o min.	...
20	357	21	173	25	68	30	40
45	172	50	105	95	33	88	24
103	100	111	64	231	26	271	19
236	83	231	42	345	19	374	18
335	82	360	38	480	15	480	10
480	75	478	34				

These results are illustrated in Fig. 1. The curves show that the after-effect is a function of the total light energy absorbed during illumination *i.e.*, number of molecules of reactant transformed. It drops off extremely rapidly the instant the light is cut off. Tables III and IV summarise the results obtained at 25°.

TABLE III.

Temperature of thermostat = 25°. Concentrations: $N/2$-$K_2C_2O_4$, $N/300$-KI, $N/1200$-I_2.

A. Dark reaction.

B. Illuminated for 15 min. and then measured the rates in the dark.

Time.	$Na_2S_2O_3$.	$K \times 10^7$.	Time.	$Na_2S_2O_3$.	$K \times 10^5$.
			o min.	1·00 cc.	..
o min.	7 15 c.c.	...	10	0·85	706
55	7·10	545	53	0·60	418
180	7·00	511	99	0·40	402
314	6·85	584	140	0·30	374
451	6·75	554	197	0·20	355

Table IV shows the effect of time of illumination at $25°$. The initial concentrations of the reactants were the same as in Table III.

TABLE IV.

Time of illumination.

15 min.		10 min.		5 min.		1 min.	
t	After-effect $K \times 10^5$.	t.	$K \times 10^6$.	t.	$K \times 10^5$.	t.	$K \times 10^5$.
o min.	...	o min	...	o min.	...	o min.	...
10	·701	15	·215	15	99	15	41
53	413	30	183	43	81	33	36
99	397	60	163	88	63	73	28
140	369	120	146	186	54	123	23
197	350	240	116	315	47	242	17
				426	39	381	16
						557	12

TABLE V.

Concentrations were the same as in Table III. The dark reaction at this temperature was immeasurably slow. Exposure to bright sunlight for 30 min. Temperature of thermostat $= 0·3°$.

Time (min.)	o	97	212	312	481
After-effect $(K \times 10^7)$	—	917	679	519	451

The figures show that there is a regular fall in the after-effect which persists for a long period. They are calculated on the unimolecular formula which holds for the normal dark reaction, but this formula is not applicable to the actual course of the after-reaction, which probably depends upon the slow disappearance of some active intermediate product. The latter may react with iodine to give the measured after-effect while decaying spontaneously in other ways. It is thus impossible to represent the total change by any simple formula. For this reason the measured rate of iodine reduction (Fig. 1) never approaches that of the normal dark reaction within the measurable time limits of the experiments.

FIG. 1

Photochemical after-effect at 50°.

Curves 1—4 show the course of after-effect obtained in the periods of illumination of
15, 10, 5 and 1 minute respectively.   Conc. same as in Table I.
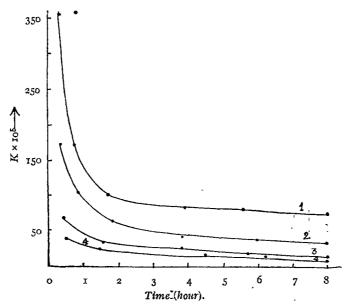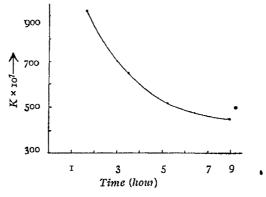
FIG. 2 .

Photochemical after-effect at 0·3°.

The conc. of the reactants same as in Table IV.

The effect of different temperatures cannot be usefully compared since
different concentrations of iodine and potassium iodide must be employed
in order to obtain convenient reaction velocities.   The latter can be regu-
lated by varying the concentrations of potassium iodide.

It is worthy of note that no measurable dark reaction was found

at $0\cdot3°$, and the after-effect curve obtained (Fig. 2) thus represents the rate of decay without this complication.

Effect of Addition of Fresh Iodine to Decolourised End Solutions of Illuminated $K_2C_2O_4 - I_2$.

We have examined in detail the effect of restoring in the dark in the original concentration the iodine completely used up in the photo-reaction (*i*) at various time intervals after decolourisation of the mixture, (*ii*) at various temperatures and (*iii*) with varying concentrations of potassium iodide.

For the sake of brevity the tables are not reproduced. The results of experiments on (*i*) at $25°$ are shown in Fig. 3.

FIG. 3

Secondary after-effect at $25°$.

Time (hours)

The curves A-H show the course of secondary after-effect obtained by the addition of fresh iodine to the solutions in which iodine had been completely reduced photochemically, immediately after the reduction had been judged to be complete and intervals of 15 mins, 30 mins, one hour, one hour 40 mins., 3 hours, 6 hours, and 12 hours from the moment of decolourisation -of- the original solutions respectively. After an interval of 24 hours. the secondary after-effect vanished and the addition of fresh iodine to this solution gave the normal dark rate of the reaction. The concentrations were the same as in Table IV.

(*i*) *Effect of Time Interval.*—It will be seen that "decay curves" are obtained similar in form to the original after-effect curves, but that the actual values of the initial velocity constants are very much less than those obtained by illumination.

. In these experiments fresh iodine was added in the dark at different intervals from the moment after the original illuminated iodine had been, judged to have been used up. The estimation of the actual intervals is therefore only approximate. The reaction velocities obtained indicate that there is a general spontaneous decay of activity in the decolourised solution extending over a period of about 24 hours, after which it is no longer detectable.

(ii) *Effect of Temperature.*—Experiments were performed at various temperatures between 25° and 50° on the "activity" of the decolourised solution, using the same concentrations of reactants in each case.

TABLE VI.

Concentrations: $N/2$-$K_2C_2O_4$, $N/300$-KI, $N/1200$-I_2.

Temperature.	Dark rate. $K_1 \times 10^5$.	Rate with added I_2. $K_2 \times 10^5$.	Activity K_2/K_1.
25°C	5	35	7·0
30	17	82	4·8
35	45	180	4·0
40	127	287	2·3
45	297	354	1·2
50	770	779	1·0

In all these experiments fresh iodine was added as soon as the decolourisation of the original mixture by illumination had been judged to be complete. The measure of "activity" has been taken as the ratio of the rate of iodine reduction, obtained one hour after the addition of fresh iodine to the decolourised solution, to the normal dark rate at a particular temperature. The rate of disappearance of added iodine, which we may call the "secondary after-effect", has been computed in the above manner in order to obtain comparable results. The data clearly show that the rate of disappearance of "activity" is a function of the temperature. It is greatest at 25°, gradually diminishing up to about 50° when no measureable effect could be detected.

A significant fact is that at 50° there is still a pronounced photochemical after-effect (Table IA and IB) in solutions partially decolourised by illumination, but that no secondary after-effect can be observed on adding fresh iodine in the dark. The "activity" has disappeared within the short interval between decolourisation and addition of fresh iodine in the dark.

(iii) *Effect of Potassium iodide Concentration.*—This is shown in Table VII where the values of the initial velocity constants after one hour from the moment of addition of fresh iodine are tabulated at four concentrations of potassium iodide. The "activity" of the decolourised solutions is seen to diminish with increasing concentrations of the latter. Potassium

iodide exerts a common inhibiting effect on (*i*) the normal dark reaction, (*ii*) the photochemical rate, as pointed out by Berthoud (*Helv. Chim. Acta*, 1924, **7**, 307), (*iii*) the photochemical after-effect, and (*iv*) the secondary after-effect.

TABLE VII.

Temperature $= 30°$. Concentrations : $N/2\text{-}K_2C_2O_4$, $N/1200\text{-}I_2$.

Conc. of KI	...	$N/300$	$N/150$	$N/100$	$N/75$
Sec. after-effect ($K_3 \times 10^5$)...		64	17	11	2

Effect of Addition of KI on the Photochemical After-effect.

The maximum photochemical after-effect was obtained in solutions containing no potassium iodide initially as shown in Table VIII.

TABLE VIII.

Temperature of thermostat $= 25°$. Concentrations : $N/2\text{-}K_2C_2O_4$, $N/1080\text{-}I_2$ (No potassium iodide).

A. Dark reaction.			B. Illuminated at the point marked.[*]			
Time	$Na_2S_2O_3$	$K \times 10^5$	Time.	$Na_2S_2O_3$	$K \times 10^5$	After-effect $K \times 10^5$
0 min.	11·95 c.c.	...	0 min.	12·00 c.c.	...	...
33	11·00	109	60	10·40	104	...
120	8·50	123	90	9·25	126	...
180	7·50	112	137·5[*]——142·5		*i.e.*, 5 min. illumination.	
210	7·10	108	142·5	2·10	...	...
240	6·75	103	145	1·75	3168	3062
272	6·50	97	150	1·70	1226	1118
308	6·35	89	166	1·40	749	643
			183	1·05	743	637
			210	0·50	545	439

From the tables,

$$\frac{\text{After effect } (t = 145 \text{ min.})}{\text{Dark rate } (t = 145 \text{ min.})} = \frac{3062}{116} = 26, \text{approximately},$$

whereas from Table IV, for the same time of pre-illumination, *i.e.*, 5 minutes

this ratio is $\frac{99}{5} = 20$ (approx.).

Thus the presence of $N/300$-KI in the latter case diminishes the relative value of the after-effect. The decreasing values of the velocity constants in Table VIIIA are due to the gradual accumulation of potassium iodide in the solution.

Free Oxalic Acid and Iodine.

Attempts were made finally to examine the reaction between free oxalic acid and iodine under nitrogen using the same source of illumination. Some measurements have appeared in the literature of the oxalic acid-iodine reaction performed in air. These are of little value on account of the photochemical reaction between aqueous HI and atmospheric oxygen. The extent to which the reaction can be examined is limited, firstly, by the small solubility of iodine in aqueous solution and secondly, by the slowness of the reaction, but it was found possible, using $N/800$-iodine, to obtain a measureable dark rate at 50° (Table IX).

TABLE IX.

Temp. of thermostat $= 50°$. Concentrations : $N/2$-$H_2C_2O_4$, $N/800$-I_2 (without KI).

A. Dark reaction.			B. Illuminated for 30 min.		
Time.	$Na_2S_2O_3$	$K \times 10^7$	Time	$Na_2S_2O_3$	$K \times 10^7$
0 min.	3·40 c.c.	...	0 min.	2·20 c.c.	...
100	3·35	650	170	2·15	588
360	3·25	545	355	2·10	577
483	3·20	547	500	2·08	506

A distinct photo-rate was found superimposed on the dark reaction which could not be measured accurately with the resources at our disposal, but it is significant that no after-effect could be observed. These latter

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experiments were done under nitrogen in a specially constructed apparatus from which all atmospheric oxygen was carefully excluded throughout the course of the experiments.

The potassium oxalate-iodine reaction itself was also examined under nitrogen. Atmospheric oxygen was found to have no effect on the kinetics.

Nature of the "Activity".

The end solutions obtained by complete reduction of iodine were found in all cases to be completely inactive towards mercuric chloride solutions in contradistinction to permanganate-treated oxalate. Experiments on the latter reaction will be described in a further communication.

A large number of experiments were performed under nitrogen in the dark, but in no case was any reaction found to take place. The failure to react was not due to the presence of potassium-iodide, since control experiments with permanganate-oxalate-iodide solutions were found to reduce mercuric chloride in the usual manner.

We are thus led to the conclusion that, the mechanism of "activation" in these two reactions is quite distinct and that they cannot be ascribed to a common activated product or to acquisition of energy, chemical and photochemical respectively, which subsequently manifests itself through the same mechanism. With iodine the experiments already described show that oxalic acid molecule as such takes no part in the reaction process, but that it is exclusively ionic in character.

DISCUSSION.

Suggestions have already been put forward about the nature of the reaction by Mukerji and Dhar (*J. Indian Chem. Soc.*, 1928, 5, 203) and Abel (*loc. cit.*). Dhar's explanation does not account for the secondary after-effect, apart from the inherent difficulty of assuming "activated" molecules to retain their energy for periods of 24 hours or more.

Abel accepts as the most likely intermediate product the oxalato-ion postulated by Berthoud which may either lose or gain an electron as indicated below :

$$2CO_2 \xleftarrow[\text{red.}]{-\ominus} \begin{matrix} COO' \\ | \\ COO \end{matrix} \xrightarrow[\text{ox.}]{+\ominus} \begin{matrix} COO' \\ | \\ COO' \end{matrix}$$

His theory does not offer any explanation for the absence of the secondary after-effect at higher temperatures found by us, when the photochemical after-effect is still quite pronounced.

It appears to us that a possible scheme may be derived by a simple extension of Berthoud's chain mechanism for the photochemical reaction (loc. cit.) as shown below.

$$I_2 + h\nu \longrightarrow 2I \qquad\qquad \ldots \quad (i)$$

$$I + I \longrightarrow I_2 \qquad\qquad \ldots \quad (ii)$$

$$I + I + I' \longrightarrow I_3' \qquad\qquad \ldots \quad (iii)$$

$$I + C_2O_4'' \longrightarrow I' + C_2O_4' \qquad\qquad \ldots \quad (iv)$$

$$C_2O_4' + I_2 \longrightarrow 2CO_2 + I + I' \qquad \ldots \quad (v)$$

$$\left.\right\} \text{chain.}$$

Both I and C_2O_4' are chain carriers and since they are assumed to be in very small stationary concentrations in the presence of a large excess of C_2O_4'' and I_2, their chances of reaction will be overwhelmingly predominant. So long as molecular iodine is present, reaction (v) will proceed slowly as revealed in the after-effect.

If we assume that in the absence of molecular iodine reaction (iv) is an instantaneously established equilibrium reaction, depending upon electronic interchange, we may write it in the form

$$I + C_2O_4'' \rightleftharpoons I' + C_2O_4' \qquad\qquad \ldots \quad (vi)$$

When fresh iodine is added to (vi) the chain is recommenced, thus accounting for the secondary after-effect.

The respective stationary concentrations of C_2O_4' and I are mainly reduced by self-combination, the rate of which increases with rise of temperature

$$C_2O_4' + C_2O_4' \longrightarrow 2CO_2 + C_2O_4'' \qquad \ldots \quad (vii)$$

$$I + I \longrightarrow I_2 \qquad\qquad \ldots \quad (viii)$$

but the chances of these reactions are small compared to (iv) and (v).

The decay of "activity" may be attributed to the falling stationary concentration of C_2O_4' in (vi) and consequent lower reaction velocity of (v), which is responsible for the removal of molecular iodine.

The increase in the after-effect rate with increasing periods of pre-illumination can be accounted for by assuming (v) to be slower than (iv), so that an excess of C_2O_4' accumulates during illumination.

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The fact that no secondary after-effect has been found at 50° may be explained on the assumption that the chances of reaction (vii) will be very much greater in the absence of I_2, and it is so fast at that temperature that the stationary concentration of C_2O_4' in (vi) becomes negligible and hence no change is observed when fresh iodine is added in the dark. With increasing time intervals before addition of iodine at lower temperature, the concentration of C_2O_4' will have been correspondingly reduced.

The same explanation holds good for the lower rate of the secondary after-effect compared to the photochemical after-effect.

The effect of addition of potassium iodide, in extension of Berthoud's original assumption for the photochemical mechanism, is to reduce the stationary concentration of I and hence of C_2O_4' in (vi) in accordance with reaction (iii). The concentration of C_2O_4 (i) is highest in light when a constant supply of fresh iodine atoms is being furnished, (ii) falls off rapidly on darkening owing to self-combination, (iii) is small when iodine is completely used up, (iv) is minimum after about 24 hours.

One of us (B.B.L.) is thankful to the Lucknow University for the grant of a Research Fellowship.

THE TERNARY SYSTEM. POTASSIUM NITRATE, AMMONIUM NITRATE AND WATER AT 25°.
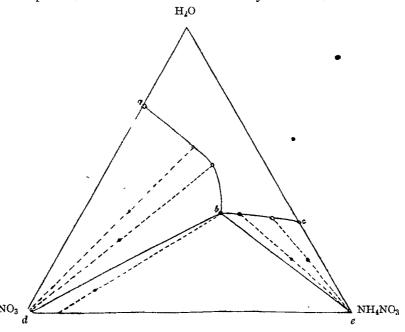
By R. K. Bahl and Surjit Singh.

In the system KNO_3-NH_4NO_3-H_2O, studied at 25°, the two salts do not form any double salt or a salt hydrate.

The heteregeneous equilibria between the nitrates of potassium and ammonium was studied to determine the existence of any double salt formed and to investigate the change of the solubility of one in the presence of the other along with the nature of the solid phases present. The vapour phase has been assumed to be absent and the whole subject has been treated from the point of view of condensed system at atmospheric pressure.

To a definite amount of potassium nitrate, increasing amounts of ammonium nitrate were added in presence of a constant amount of water. The various complexes were vigorousliy stirred up to equilibrium in wide tubes immersed in a water thermostat kept at a constant temperature of 25°. The usual time given was 48 hours. When the equilibrium was established, the composition of the solution was determined by withdrawing portions of them by means of a pipette heated previously to the temperature of the bath. It was filtered and weighed in stoppered bottles and then analysed. The moist residue was weighed separately and analysed.

The ammonium ion was estimated by the usual distillation method and the nitrate was determined by Lunge's nitrometer as given by Scott ("Standard Methods of Chemical Analysis", 1925, Vol. I p. 353). The amounts of potassium and water were calculated by difference.

The system at 25° is shown in Fig. 1 and the data for this system at the above temperature is given below.

Composition by Weight.

Temperature = 25°

Solution.		Rest		
KNO$_3$.	NH$_4$NO$_3$	KNO$_3$	NH$_4$NO$_3$	Solid phases
27·1 %	0 %	—	—	KNO$_3$
19·36	22·80	50·22%	14·25%	KNO$_3$
16·56	31·784	58·15	16·31	KNO$_3$
22·21	42·83	74·4	17·8	KNO$_3$, NH$_4$NO$_3$
16·92	48·20	9·1	72 1	NH$_4$NO$_3$
7·23	59·44	4·3	77·2	NH$_4$NO$_3$
0	68·1	—	—	NH$_4$NO$_3$

It is clear from the above that the system potassium nitrate-ammonium nitrate-water belongs to the simplest type of ternary system; neither double salts nor salt hydrates occur in it.

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THE SULPHONATION OF MONOETHYLANILINE

By G. V. Shirolkar, I S. Uppal, and K. Venkataraman.

The sulphonation of monoethylaniline and the N-ethylation of p-toluene-sulphonyl-sulphanilic, metanilic and orthanilic acids, has been studied and it has been found that the sulphonation proceeds exactly as in the case of monomethylaniline.

While preparing certain wetting agents by condensing oleic acid with N-methylsulphanilic acid (Dhingra, Uppal and Venkataraman, *J. Soc. Dyers & Col.*, 1936, **52**, 91), the constitution of the latter as the *para* compound was assumed. In view of the somewhat conflicting nature of the existing evidence regarding the three monomethylaniline sulphonic acids, proof of their orientation was later adduced (Uppal and Venkataraman, *J. Soc. Chem. Ind.*, 1938, **57**, 410). Sulphonation of monomethylaniline leads according to the conditions of sulphonation, to N-methylsulphanilic acid or a mixture of this acid and N-methyl-metanilic acid. N-methyl-orthanilic acid has been obtained by the methylation of orthanilic acid with dimethyl sulphate. The three monomethylaniline sulphonic acids are characterised as the arylamine salts of their p-toluenesulphonyl derivatives, the latter being prepared both by treating the monomethylaniline sulphonic acids with p-toluenesulphonyl chloride and by the N-methylation of p-toluenesulphonyl-sulphanilic, metanilic and orthanilic acids. Halberkann (*Ber.*, 1921, **54**, 1836) established the position of the sulphonic group in N-methylsulphanil c acid by preparing its p-toluenesulphonyl derivative and comparing it with the product of the methylation of N-p-toluenesulphonylsulphanilic acid.

Studying the sulphonation of monoethylaniline and the N-ethylation of p-toluenesulphonyl-sulphanilic, metanilic and orthanilic acids on parallel lines, it has been found that the sulphonation proceeds exactly as in the case of monoethylaniline.

The preparation of N-ethylsulphanilic acid (I) was described in G.P.

EtHN⟨benzene ring⟩SO₃H   EtHN⟨benzene ring⟩SO₃H   EtHN⟨benzene ring⟩SO₃H

$$EtHN-C_6H_4-SO_3H \qquad EtHN-C_6H_4-SO_3H \qquad EtHN-C_6H_4-SO_3H$$

(I)   (II)

295, 104 (1916); monoethylaniline was slowly added in the cold to sulphuric acid monohydrate, followed by the gradual addition of 80% fuming

sulphuric acid, the whole mixture being heated at 150-70° for about 2—3 hours, till there was no trace of free base. The m.p. of the substance was not quoted.

In *G.P.* 48, 151 (1889) the preparation of *N*-ethyl-metanilic acid (II) has been claimed by direct ethylation of metanilic acid. Gnehm and Scheutz (*J. pr. Chem.*, 1901, ii, **63**, 414) prepared the same acid (II) (decomposing at 294°). These authors sulphonated ethylaniline by adding it to double the required amount of 25% fuming sulphuric acid and then adding 3 times the weight of 75% fuming acid, the temperature being kept below 50°. After dilution and working up in the manner described, (II) was obtained in needles, the substance (I) accompanying it in small amounts.

No attempts have been recorded in the literature regarding the preparation of *N*-ethyl-orthanilic acid (III).

The sulphonation of monoethylaniline with 20% fuming sulphuric acid at 185-90° leads to a single product, decomposing at 259°, identified as the *p*-acid (I). When the base is sulphonated at 50°, using 80% fuming sulphuric acid in the later stages of the reaction, the product is a mixture of the *m*-acid (II) (decomp. 286°) and the *p*-acid (I) (decomp. 259°) (*cf.* Gnehm and Scheutz, *loc. cit.*). Keeping the temperature at or below 50°, the proportion of the two acids appeared to depend on the strength of the sulphuric acid. Under our conditions the formation of the *p*-acid is about twice as much as that of the *m*-acid, although the actual quantity of the pure *p*-acid isolated is smaller on account of the repeated crystallisation necessary for complete purification. The course of the reactions under the various conditions described is, therefore, precisely parallel to the course of the reactions in the case of monomethylaniline (*loc. cit*).

On ethylating orthanilic acid with diethylsulphate (*cf.* Houben and Schreiber, *Ber.*, 1920, **53**, 2346) the *o*-acid (III) is obtained (decomp. 212-13°). As in the case of the monomethylaniline sulphonic acids, the three isomers have been oriented by an application of Halberkann s method (*loc. cit.*). Each of the three aniline sulphonic acids is converted into its *N*-*p*-toluenesulphonyl derivative (*e.g.* IV) which is ethylated with

$$\text{Me}\langle\quad\rangle\text{SO}_2\text{NH}\langle\quad\rangle\}\text{SO}_3\text{H}$$

(IV)

diethylsulphate and sodium hydroxide to yield the corresponding *N*-ethyl derivative (V).

$$Me\!\!\left<\!\!\!\bigcirc\!\!\!\right>\!\!SO_2\!\cdot\!NEt\!\!\left<\!\!\!\bigcirc\!\!\!\right>\!\!\}SO_3H$$

(V)

The three *N*-ethylaniline-sulphonic acids have been condensed with *p*-toluenesulphonyl chloride and the products compared with those referred to above. As the free acids are not readily isolable the actual comparison made is of the arylamine salts (Forster and Keyworth, *J. Soc. Chem. Ind.*, 1924, **43**, 165T), the *p*-chloroaniline salt being convenient to use.

EXPERIMENTAL.

·N-*Ethylsulphanilic Acid* (I).—To fuming· sulphuric acid (20%; 150 g.) contained in a 200 c.c. wide-mouthed round-bottomed flask fitted with an air condenser and a calcium chloride tube, monoethylaniline (50 g.) was slowly added through the condenser and the mixture heated in an oil-bath at 190° for 4 hours. The dark coloured mixture, after cooling, was gently poured into ice-cold acetone (2 litres) with occasional stirring and kept in the refrigerator overnight. The dark solid mass (65 g.) was collected at the pump and washed with more of acetone, till the filtrate was practically colourless.

The crude product was recrystallised (Norit) from the minimum amount of water (about 200 c.c.), filtered at the pump, washed with water till free from sulphuric acid and dried at 110°, m.p. 259° (decomp.). The final yield was 22 g. Much of the acid dissolved in cold water during the removal of sulphuric acid. The pure product after further recrystallisation from thrice the amount of water had unchanged m.p.

N-*Ethyl-metanilic Acid* (II).—The method followed was the same as in the case of *N*-methyl-metanilic acid (*loc. cit.*). Monoethylaniline (50 g) was added slowly to ice-cold and mechanically agitated fuming sulphuric acid (20%, 100 g.) at such a rate that the temperature of the reaction mixture did not rise above 50°. When the whole of the ethylaniline had been added, the temperature was raised to 60° which was maintained for 15 minutes. The flask was again externally cooled and fuming sulphuric acid (80%, 150 g.) was run in, keeping the temperature

below 40°. The mixture was kept at this temperature for about 30 minutes (till it gave a clear-solution in alkaline water) and then poured with stirring into ice-cold acetone (2 litres) and kept overnight in the refrigerator. The yellow solid (66 g.) was filtered at the pump, washed with acetone and dried at 110°. The crude product was recrystallised from water (Norit), collected on the pump, and washed with ice-cold water till free from sulphuric acid, colourless crystals, m.p. 252°, (decomp.) yield 36 g. After recrystallisation from 120 c.c. of water at room temperature, 16 g. of crystals (decomp. at 286°) were obtained, and on further recrystallisation the m.p. remained unchanged.

On concentrating all the mother-liquors and recrystallising the solid obtained therefrom, 30 g. of the product free from sulphuric acid and decomposing at 247° were obtained ; this product on repeated fractional crystallisation giving 8 g. more of the ethyl-metanilic acid (decomp. 286°). From the mother-liquor 15 g. of ethylsulphanilic acid were recovered. Its identity with the p-acid obtained in the previous experiment was proved by conversion in to the p-toluenesulphonyl derivative and its p-chloroaniline salt (vide infra).

N-*Ethyl-orthanilic Acid* (III).—Orthanilic acid (5 g.) and sodium carbonate (1·6 g.) were dissolved in warm water (20 c.c.) and the solution shaken with diethylsulphate (8 c.c.). The mixture was heated on the water-bath for 1 hour and the clear red solution concentrated to a small bulk and cooled. The precipitate (2 g.) was collected and washed with alcohol. On recrystallisation from water the product melted at 212-13° (decomp.). (Purity by titration, 99·9%).

p-*Chloroaniline Salt* (VI) *of* p-*Toluenesulphonyl-N-ethylsulphanilic Acid* (V).—N-Ethylsulphanilic acid (5 g., decomp. 259°), p-toluenesulphonyl chloride (4·8 g.) and pyridine (15 c.c.) were heated together in an oil-bath at 140° for 3 hours. The mixture was then dissolved in water and neutralised with caustic soda solution (33·9 c.c. of 1·8N), the pyridine boiled off and the solution reduced to a small bulk. On acidifying with hydrochloric acid and cooling, the product which separated was collected and crystallised from alcohol. It was then converted into the p-chloroaniline salt by the addition of p-chloroaniline hydrochloride, the precipitated salt filtered at the pump and washed with cold water to remove traces of hydrochloric acid and free p-chloroaniline hydrochloride. The m.p. was 217-18° after drying at 110°. (0·1572 G. required 3·2 c.c. of N/10-caustic soda. Calc. 3·25 c.c. ; purity 98·5%).

Ethylation of p-*Toluenesulphonylsulphanilic Acid* (IV).—The pyridine salt (6 g.) of *p*-toluenesulphonylsulphanilic acid was neutralised with sodium hydroxide (phenolphthalein), the pyridine boiled off, and the residue cooled and shaken with diethylsulphate (5 c.c.) for about 10 minutes. The mixture was then heated on the water-bath and treated alternately with 10% sodium hydroxide solution and diethylsulphate till ethylation was complete. On cooling and acidifying the reaction mixture with hydrochloric acid no precipitate separated, and the product was isolated as the *p*-chloroaniline salt by adding *p*-chloroaniline hydrochloride. The m.p. of the crystallised product and the mixed m.p. with (VI) was 217°. (0·1894 G. required 3·9 c.c. of N/10-caustic soda solution Calc. 3·92 c.c. ; purity 99·5%).

p-Chloroaniline Salt of p-*Toluenesulphonyl-N-ethyl-metanilic Acid.*—N-Ethyl-metanilic acid was condensed with *p*-toluenesulphonyl chloride and the *p*-chloroaniline salt (VII) isolated directly as above. The m.p. was 111°. (0·2412 G. required 5 c.c. of N/10-caustic soda. Calc. 5 c.c. ; purity 100%.)

Ethylation of p-*Toluenesulphonyl-metanilic Acid.*—The condensation mixture of metanilic acid (5 g.) and *p*-toluenesulphonyl chloride (5·5 g.) was neutralised, the pyridine removed as usual and the mixture ethylated with diethylsulphate (25 c.c.) and caustic soda solution (10%, 150 c.c.) as in the ethylation of *p*-toluenesulphonylsulphanilic acid, and finally the product was isolated as the *p*-chloroaniline salt. On adding *p*-chloroaniline hydrochloride, an oily mass settled down, which, on standing for some time in the refrigerator, solidified. 0·1428 G. required 2·95 c.c. of N/10-caustic soda solution. Calc. 2·96 c.c. ; purity 99 6%. The salt melted at 111° (mixed m.p. with VII was 111°).

p-Chloroaniline Salt of p-*Toluenesulphonyl-N-ethyl-orthanilic Acid*—On condensing N-ethyl-orthanilic acid with *p*-toluesulphonyl chloride as above, and converting into the *p*-chloroaniline salt, the latter, after recrystallisation, melted at 181-83°.

Ethylation of p-*Toluenesulphonyl-orthanilic Acid*—The sodium salt of *p*-toluenesulphonyl-orthanilic acid (2 g.) was dissolved in a small amount of water and ethylated with diethylsulphate (15 c.c.) and caustic soda solution (10%, 40 c.c.) heating the mixture on the water-bath for 90 minutes. The mixture was cooled and acidified with hydrochloric acid, but no product separated. On adding excess of *p*-chloroaniline hydrochloride

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solution, the oily mass, which first separated contained the unethylated substance, as it did not give a sharp end-point when titrated against caustic soda solution. On keeping the mother-liquor overnight in the refrigerator, the N-ethyl derivative, giving a sharp end-point, was obtained. 0·1338 G. required 2 8 c.c. of $N/$10-caustic soda solution. Calc. 2·8 c.c. It melted at 183°, undepressed by admixture with the previously prepared substance.

We wish to thank the University of Bombay for a research fellowship awarded to one of us.

CHEMOTHERAPY OF MALARIA. 6-METHOXYQUINOLINE-8-HYDRAZINE AND SYNTHESIS OF SOME HETERO-CYCLIC COMPOUNDS FROM IT.*

By B. K. Nandi.

Starting from 6-methoxyquinoline- 8-hydrazine a few heterocyclic compounds *e g.*, thiazole, benzopyrrole, pyrazolone and a pyrrole have been prepared. Some of the compounds have been found to be ineffective against avian malaria.

Plasmoquine, synthesised by Schulemann *et al* (*Klin. Woch.*,1932, 9, 381), is a 6-methoxy-8-aminoquinoline derivative. Several derivatives of this substance have been made with different side-chains to find out a more suitable antimalarial drug with less toxicity. In this paper 6-methoxy-8-aminoquinoline has been converted into 6-methoxyquinoline-8-hydrazine by following the method described by Dufton (*J. Chem. Soc.*, 1891, 59, 757 ; 1892, 61, 785). This quinolylhydrazine is then condensed with various ketones, thiocyanate, etc. giving a thiazole, benzopyrrole, pyrazolone and a pyrrole derivative. Thus by the interaction of 6-methoxyquinoline-8-hydrazine with potassium thiocyanate 6-methoxyquinoline-8-thiosemicarbazide is obtained which after condensation with ω-bromo—acetophenone gives 2-(6'-methoxy-8'-hydrazinoquinolyl)-4-phenylthiazole (I, R = methoxy quinolyl. *cf.* Bose and Nandi, *J. Indian Chem. Soc.*, 1930, 7, 733). The condensation with *cyclo*hexanone and subsequent treatment with dilute sulphuric acid gives 6'-methoxyquinolino-(7': 8': 2 : 3)-tetrahydrobenzopyrrole (II) (Borsche, Witte and Bothe, *Annalen*, 1908, 359, 49). Similarly the condensation product with ethyl acetoacetate is (*cf.* Knorr, *Annalen*, 1887, 238, 147) 1-[8'-(6'-methoxyquinolyl)]-3-methyl-5-pyrazolone (III). A pyrrole synthesis has been effected by condensing the quinolylhydrazine with pyruvic acid and the product on treatment with concentrated hydrochloric acid gives 6'-methoxyquinolino-(7': 8': 2 : 3)-pyrrole-5-carboxylic acid (IV) with remarkable ease (Dufton, *J. Chem. Soc.*, 1892, 786). The quinolylhydrazine has also been condensed with potassium cyanate and *dl*-arabinose to make respectively 6-methoxyquinoline-8-semicarbazide and 6-methoxy-8-quinolyl-hydrazone of arabinose.

Some of these compounds have been tested against avian malaria without any effect. Only 6-methoxyquinoline-8-hydrazine retains some

activity against paramaecia which is, however, decidedly weaker than 6-methoxy-8-aminoquinoline.

R—NH—NH—C / S \ CH
N \ C·C₆H₅

(I)

MeO
CH₂
H₂C
H₂C
CH₂
N
NH

(II)

HN / N.R \ CO
MeC == CH

(III)

R = methoxyquinolyl,

MeO
N

HC
HOOC·C
N
NH
MeO

(IV)

EXPERIMENTAL.

6-Methoxyquinoline-8-hydrazine.—6-Methoxy-8-aminoquinoline (20 g.) in hydrochloric acid (100 c.c., 22%) was diazotised at 0° with sodium nitrite (9·5 g.). The diazotised solution was quickly filtered and left at 0°. The stanno-chloride of the hydrazine was at once precipitated when 75 g. of stannous chloride in hydrochloric acid were added. After keeping for an hour in the cold the precipitate was collected and dissolved in sufficient boiling water and the tin precipitated by hydrogen sulphide. The filtrate was evaporated down considerably and the free hydrazine was precipitated by sodium hydroxide. It crystallised from hot water in fine, long slender needles, m.p. 67°. (Found: C, 63·11; H, 5·93; N, 22·40. $C_{10}H_{11}ON_3$ requires C, 63·48; H, 5·82; N, 22·22 per cent).

1-(6'-Methoxyquinoline)-8'-thiosemicarbazide.—Equimolecular proportions of 6-methoxyquinoline-8-hydrazine and potassium thiocyanate were dissolved in dilute hydrochloric acid and water respectively. After

the addition of thiocyanate solution to the former, the mixture was boiled for 15 minutes. After cooling, the solution was made alkaline with sodium hydroxide and the thiosemicarbazide collected and crystallised from alcohol, m.p. 259-61° (Found: N, 22·51; S, 12·67. $C_{11}H_{12}ON_4S$ requires N, 22·58; S, 12·90 per cent).

2- (6'-*Methoxy-8'-hydrazinoquinolyl*) - 4 - *phenylthiazole.* — 6- Methoxyquinoline- 8-thiosemicarbazide (6 g.) and ω-bromoacetophenone (5 g.) were dissolved in alcohol and heated under reflux on the water-bath for about 1½ hours. The solution was then made strongly alkaline with sodium hydroxide and the precipitated thiazole collected, washed well with water, and crystallised from alcohol, m.p. 121-24°, yield 20%. (Found: N, 16·31; S, 8·88. $C_{19}H_{16}ON_4S$ requires N, 16·09; S, 9·19 per cent).

6-*Methoxyquinoline*-8-*hydrazone* of cyclo*Hexanone.*—6-Methoxyquinoline- 8-hydrazine (4 g.), dissolved in glacial acetic acid (10 c c.) and diluted to 30 c.c., was mixed with a solution of cyclohexanone (2 g.), dissolved in 20 c.c. of alcohol, when an oil separated. After warming on the water·bath for a few minutes it was allowed to stand, when the oil solidified on scratching. The product crystallises from dilute alcohol in shining pale green needles, m.p. 91°. (Found: N, 15·76. $C_{16}H_{19}ON_3$ requires N, 15·61 per cent).

6'-*Methoxyquinolino*-(7':8':2:3)-*tetrahydrobenzopyrrole.*—The 6-methoxyquinoline- 8-hydrazone of cyclohexanone passes easily into the benzopyrrole on heating in dilute sulphuric acid for a few minutes on the waterbath. The yellow sulphate of the benzopyrrole was suspended in water, made alkaline and extracted with ether in which it dissolves on prolonged shaking. On slow evaporation of ether the benzopyrrole crystallised out in ·colourless plates, m.p 181-82°. The sulphate of the benzopyrrole is fluorescent in alcohol and chloroform. The hydrochloride of the base was obtained as yellow crystals by passing hydrogen chloride in ethereal solution, m.p. 256-59°. (Found: C 75·97; H 6·25; N, 11·28. $C_{16}H_{16}ON_2$ requires C, 76·19; H, 6·34; N, 11·11 per cent).

1- [8'- (6'-*Methoxyquinolyl*)]-3-*methyl-5-pyrazolone.*—A mixture of 6-methoxyquinoline-8·hydrazine (3·2 g.) and ethyl acetoacetate (2·8 g.) was heated on the steam-bath for 2—3 hours. The deep coloured product solidified on cooling and scratching and was crystallised from ligroin (b.p. 80-110°), m.p. 72°. This crystallised product was then heated on the steam-bath for nearly 8 hours when it was converted into the pyrazolone. The *pyrazolone* also crystallised from ligroin, m.p. 135°. (Found: C, 65·72; H, 4·68; N, 16·39. $C_{14}H_{13}O_2N_3$ requires C, 66·14; H, 4·72; N, 16·53 per cent).

6'-Methoxyquinoline- (7' : 8' : 2 : 3) *-pyrrole-5-carboxylic Acid.*—On adding pyruvic acid to a concentrated aqueous solution of 6-methoxyquino-line-8-hydrazine hydrochloride in molecular proportions, the mixture became almost solid due to the separation of the hydrochloride of the pyruvic acid hydrazone This substance was crystallised from• water. The pyrrole condensation takes place with remarkable ease when the pyruvic acid quinolylhydrazone was boiled for about an hour with concentrated hydrochloric acid. The liquid darkened and became filled with yellow crystals of the hydrochloride of the pyrrole acid. The free acid was precipitated by making the aqueous solution of the hydrochloride neutral to litmus or by diluting the aqueous solution considerably. It was then crystallised by dissolving in water with a little ammonia and allowing to evaporate in a dish on the water-bath. As the ammonia was driven off, the acid crystallised in beautiful yellow needles. m.p. 197-98°. It is sparingly soluble in alcohol. (Found: C 64·07; H, 4·32; N, 11·44. $C_{13}H_{10}O_3N_2$ requires C, 64·46; H, 4·13; N, 11·57 per cent).

1- (6'-*Methoxyquinoline*)- 8'-*semicarbazide* (*cf.* Dufton, *loc. cit.*).—The precipitate, as obtained following Dufton, was dissolved in water and the solution made alkaline. The free semicarbazide was crystallised from alcohol, m.p. 236-39° (softening from 225°). (Found : N, 23·95. $C_{11}H_{12}O_2N_4$ requires N, 24·13 per cent).

6-*Methoxyquinoline*- 8-*hydrazone of Arabinose.*—6-Methoxyquinoline-8-hydrazine (0·5 g.), dissolved in dilute acetic acid (5 c.c.), was mixed with an aqueous solution of arabinose (0·45 g.) and the mixture warmed on the water-bath for a few minutes. The hydrazone separated on scratching and was crystallised from water in pale green needles, m.p. 140°. (Found : N, 12·87. $C_{15}H_{19}O_5N_3$ requires N, 13·08 per cent).

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SYNTHETIC INVESTIGATIONS ON DEGRADATION PRODUCTS OF BILE ACIDS, SEX HORMONES, Etc. PART II. A SYNTHESIS OF KETO-DEOXY-OESTRIC ACID.

By D. K. BANERJEE.

By the extension of the method for the preparation of 7-methyl-o:3·3-bi*cyclo*-octanone, a synthesis of 9-keto-deoxyoestric has been described. It is interesting to note that the above method can be suitably applied for the synthesis of 1:2-di-substituted phenanthrenes.

In a previous paper (*J. Indian Chem. Soc.*, 1940, **17**, 423) a method for the synthesis of 7-methyl-o : 3 : 3-bi*cyclo*octane-1-one has been described, where the *trans*-form of the above compound has been found to predominate. The locking of the fused carbon rings in the 8-methylhydrindan-1-one portion of the sex hormone molecules is believed to be *trans*. It, therefore, appeared to be of interest to investigate the results of application of a similar method for the synthesis of simple 8-methylhydrindan-1-one. All the synthetical methods (Chuang, Tien and Ma, *Ber.*, 1936, **69**, 1494 ; Kon, Linstead and Simons, *J. Chem. Soc.*, 1937, 814 ; Robinson and Walker, *ibid.*, 1937, 60, 1160), so far described by different workers for its preparation, have led to the formation mainly of the *cis*-isomeride (*cf.* Linstead, Millidge and Walpole, *J. Chem. Soc.*, 1937, 1142 ; Linstead and Millidge, *ibid.*, 1936, 480). But the fact that *iso*lithobilianic acid and allo-*iso*lithobilianic acid, which differ only in stereochemical configuration, give rise on thermal decomposition to two different pyro-acids and desoxopyro-acids (Windaus, Hückel and Reverey, *Ber.*, 1923, **56**, 91 ; Windaus, *Annalen*, 1926, **447**, 233, 240) and further a recent synthesis of equilenin from a *trans*-dicarboxylic ester by Bachmann, Coie and Wilds (*J. Amer. Chem. Soc.*, 1939, **61**, 974) must be considered as very encouraging,

An examination of the tricarboxylic ester (III), which was prepared by the condensation of ethyl cyanoacetate with ethyl γ-acetylbutyrate according to the method of Cope (*J. Amer. Chem. Soc.*, 1937, **59**, 2327) followed by the addition of hydrocyanic acid to the unsaturated cyano-ester (I) by the method of Hope and Sheldon (*J. Chem. Soc.*, 1922, **121**, 2223) and subsequent hydrolysis and esterification of the resulting dicyano-ester (II), made it evident that on cyclisation it could give rise to three different cyclic compounds (IV, R=H ; R′=CO_2Et), (V) and (VI).

CH₃ structures:

$$CH_3$$
$$C.[CH_2]_3 \cdot CO_2Et$$
$$\|$$
$$C(CN) \cdot CO_2Et$$

(I)

$\rightarrow$

$$CH_3$$
$$NC \cdot C \cdot [CH_2]_3 \cdot CO_2Et$$
$$|$$
$$CH(CN) \cdot CO_2Et$$

(II)

$\rightarrow$

$$CH_3$$
$$EtO_2C.C \cdot [CH_2]_2 \cdot \overset{*}{CH_2} \cdot CO_2Et$$
$$|$$
$$CH_2 \cdot CO_2Et$$

(III)

$\rightarrow$

(IV)

(VI)

(V)

Actual cyclisation of (III) has now been effected and investigations, which are in progress to determine the manner in which the ring-closure has taken place, will be the subject of a future communication.

Meanwhile it seemed quite obvious that if the C-atom marked (*) in the tricarboxylic ester (III) be substituted then the ring-closure can take place in only one way and the product (VII) can be expected to give rise to a compound of the type (VIII) by following similar reactions as employed in the case of 7-methyl-o-3 : 3-bicyclooctane-1-one (loc. cit.).

(VII)

(VIII)

Further if R in (VII) be phenyl or a p-methoxyphenyl group then the sodio-salt of the β-ketonic ester (VII) on condensation with ethyl bromo-

acetate or with ethyl β-chloropropionate followed by hydrolysis and esterification should give rise to keto-esters of the types (IV, R =, X=H OH or OMe ; R′=CH$_2$·CO$_2$Et or CH$_2$·CH$_2$·CO$_2$Et), which by the application of Cook's method of phenanthrene synthesis (*J. Chem. Soc.*, 1936, 76 should result in the formation of the dicarboxylic acids (IX, R=H, OH or OMe ; R′=CO$_2$H or CH$_2$·CO$_2$H).

(IX)

Robinson has suggested the names oestric acid and homooestric acid for the above two dicarboxylic acids, which were first obtained by Marian and Haslewood (*J. Soc. Chem. Ind.*, 1932, **51**, 2777 ; *cf.* MacCorquodale, Thayer and Doisy, *J. Biol. Chem.*, 1933, **99**, 327) from oestriol and by Bardhan (*J. Chem. Soc.*, 1936, 1848), from o-methyloestrone respectively.   Later both of these were prepared by Robinson (*J. Chem. Soc.*, 1938, 1997) by different methods.   A synthesis of isomeric mixture of o-methyloestric - acid has also been described by Robinson and Walker (*ibid.*, 1938, 183).

In the present communication a synthesis of keto-deoxyoestric acid (XVI) on the above lines, has been described.   Considerable progress has also been made in the synthesis of oestric acid and the homo-oestric acid starting with the p-methoxyphenyl compound and this will be the subject of the next communication.

Sodio-ethyl phenylcyanoacetate has been condensed with β-chloroethyl-methylketone to yield ethyl a-cyano-a-phenyl-γ-acetylbutyrate (X), which is hydrolysed when a-phenyl-γ-acetylbutyric acid (XI) is obtained as a liquid. The ethyl ester of the above acid is condensed with ethyl cyanoacetate as before to yield the unsaturated cyano-ester (XII). On addition of hydrogen cyanide to (XII), the dicyano-ester (XIII) is obtained as an extremely viscous liquid. This is hydrolysed in the crude state to yield a-phenyl-δ-methyl-δ-carboxypimelic acid (XIV), the triethyl ester of which undergoes cyclisation by sodium in benzene solution. The resulting β-ketonic ester (IV, R=Ph ; R′ = CO$_2$Et) could not, however, be distilled in vacuum

5

without decomposition, so that the sodio-salt of the above β-ketonic ester formed-by Diekmann's condensation is treated with ethyl bromoacetate in the crude state and in another experiment potassium salt of the same β-ketonic ester, which is somewhat decomposed during distillation, has been condensed with ethyl β-chloropropionate, and in each case the resulting crude product is hydrolysed and subsequently esterified to yield ethyl 1-keto-3-methyl-3-carbethoxy-6-phenyl*cyclo*hexane-2-acetate (IV, R=Ph; R'=CH$_2$ CO$_2$Et) and ethyl 1-keto-3-methyl-3-carbethoxy-6-phenyl-*cyclo*hexane-2-β-propionate (IV, R=Ph; R'=CH$_2$·CH·CO$_2$Et) respectively together with some ethyl 3-methyl-6-phenyl*cyclo*hexanone-3- carboxylate in the lower boiling fractions. The diester (IV, R=Ph; R'=CH$_2$ CO$_2$Et) is treated with zinc wool and ethyl bromoacetate in toluene solution. The analytical data and molecular weight determination of the higher boiling fraction of the resulting product show that it consists mainly of the unsaturated ester (XV). The above compound on treatment with an exeess of red phosphorus and hydriodic acid yields a resinous un-crystallisable acidic product, which undergoes cyclisation with elimination of water by means of concentrated sulphuric acid to give the keto-dibasic acid (XVI) as a thick gum. The above acid, however, gives a semicarbazone, which after crystallisation from dilute methyl alcohol remained somewhat coloured and melted at 165-75^{c}.

(XV) → (XVI)

EXPERIMENTAL

Ethyl 1-cyano-2-methyl-Δ^1-pentene-1 : 5-dicarboxylate (I).—Ethyl-·-acetyl butyrate (67 g.), ethyl cyanoacetate (46 g.), acetamide (9 g.) and glacial acetic acid (100 c.c.) (*cf.* Cope, *loc. cit.*) were taken in a Claisen s flask and slowly distilled. A little more than 100 c.c. of a distillate was collected in course of 6 hours, the temperature of the distilling vapours being kept between 110 and 115°. The reaction product was taken up in ether and the ethereal · solution well washed · with water. The ether was removed and the residue fractionated, and the unsaturated cyano-ester (70· g.) collected at 175-78°/7·5 mm. or 155·60°/3 mm.•(Found : N, 5·8. $C_{13}H_{19}O_4N$ requires N, 5·53 per cent).

Diethyl 1:2-Dicyano-2-methylpimelate (II).—A solution of potassium cyanide (38 g) in water (206 c.c) was slowly added to a solution of the above unsaturated cyano-ester (75 g.) in alcohol (300 c.c.) and water (15 c.c). The clear mixture was cooled in ice-water and treated with hydrochloric acid (d 1·15, 46·5 c.c.) diluted with water (32 c.c.) and left at the ordinary temperature for ½ hour. It was then acidified with dilute hydrochloric acid. The dicyano-ester, which separated as a thick oil, was extracted with ether. The ethereal layer was washed with water, dried, the ether removed and the residual oil distilled at 192-93°/4 mm., yield 69 g. (Found: N, 10·2. $C_{14}H_{20}O_4N_2$ requires N, 10·0 per cent).

Diethyl 2-Methyl-2-carbethoxypimelate (III).—The dicyono-ester (II) (54 g.) was hydrolysed by boiling with concentrated hydrochloric acid (380 c.c.) for 12 hours when a clear solution resulted. The crude tricarboxylic acid (25 g.) was obtained by repeatedly extracting the above acid solution, saturated with sodium chloride, with ether and after subsequent evaporation of the well-dried ethereal solution it was esterified by refluxing with a mixture of absolute alcohol (250 c.c.) and sulphuric acid (d 1·84, 40 c.c.) for 36 hours Ice-water was added to the cooled solution and the precipitated oil was taken up in ether. The ethereal layer was washed with water, sodium bicarbonate solution and then again with water and finally dried. On removal of ether, the residue boiled at 168°/6 mm. or 154-55°/3·5 mm., yield 26 g. (Found : C, 59·4 ; H, 8·5. $C_{15}H_{26}O_6$ requires C, 59·6 ; H, 8·6 per cent).

Cyclisation of the Tricarboxylic Ester (III).—A mixture of sodium dust (3·8 g.) diethyl 2-methyl-2-carbethoxypimelate (25·3 g.) in benzene (75 c.c.) was refluxed for 4 hours on the water-bath, when the whole of the sodium went into solution. The reaction mixture, on cooling, was acidified with cold dilute hydrochloric acid The benzene layer was separated, washed with dilute sodium bicarbonate solution and then with water and dried. The benzene was removed and the residue distilled at 156°/7 mm. or 140-42°/4 mm. (Found : C, 61·2; H, 7·6. $C_{13}H_{20}O_5$ requires C, 60·94; H, 7·8 per cent).

Condensation of β-Chloroethylmethyl ketone with Sodio-ethylphenyl cyanoacetate.—β-Chloroethylmethyl-ketone was prepared, according to the method described in B. P. No 282,412 (Scherring-Kahlbaum) from ethylene and acetyl chloride in presence of aluminium chloride. Ethyl phenylcyanoacetate was prepared by condensation of diethyl carbonate with benzyl cyanide (Hessler, *Amer. Chem. J.*, **32**, 120). Ethyl phenylcyanoacetate (99 g.) was slowly added to a suspension of sodium dust (12·2 g.) in dry benzene (300 c.c.) in the cold and the mixture left overnight. The mixture was refluxed on the water-bath with β-chloroethylmethyl ketone (60 g.) for 24 hours, at the end of which period the reaction mixture was cooled and treated with water. The benzene layer was separated, washed with water, and dried. The benzene was removed and ethyl α-cyano-α-phenyl-γ-acetyl butyrate (X) (115 g.) was collected at 172-75°/5 mm. (Found : N, 5·5. $C_{15}H_{17}O_3N$ requires N, 5·4 per cent).

The *semicarbazone*, prepared in the usual manner, on crystallisation from ethyl alcohol melted at 154-55°. (Found : N, 17·9. $C_{16}H_{20}O_3N_4$ requires N, 17·7 per cent).

α-Phenyl-γ-acetylbutyric Acid (XI).—The above ketocyano-ester (112 g.) was refluxed with concentrated hydrochloric acid (380 c.c.) for 20 hours. The keto-acid, which separated as an oil, was extracted with ether. The ethereal layer was treated with sodium bicarbonate solution, the alkaline solution acidified and the liberated oil extracted with ether The ethereal layer was dried and after removing ether α-phenyl-γ-acetylbutyric acid was collected at 195-97°/6 mm., yield 70 g (Found: C, 69·4 ; H, 7·2. $C_{12}H_{14}O_3$ requires C, 69·9 : H, 6·8 per cent).

Ethyl α-Phenyl-γ-acetylbutyrate was obtained by refluxing α-phenyl-γ-acetylbutyric acid (65 g.) with absolute alcohol (150 c.c.) and sulphuric acid (*d* 1·4, 8 c.c.) for 12 hours. The ester was worked up in the usual manner and was collected at 143-45°/4·5 mm., yield 67 g. (Found. C, 72·1; H, 7·7 $C_{14}H_{18}O_3$ requires C, 71·8 ; H, 7·7 per cent).

The *semicarbazone*, prepared in the usual manner, on crystallisation from dilute ethyl alcohol melted at 119-20°. (Found: N, 14·3 $C_{15}H_{21}O_3N_3$ requires N, 14·4 per cent).

Ethyl 1-Cyano-2-methyl-5-phenyl-Δ^1-pentene-1:5-dicarboxylate (XII).— A mixture of ethyl α-phenyl-γ-acetylbutyrate (29 g.), ethyl cyanoacetate (14 g.), acetamide (5 g.) and glacial acetic acid (55 c.c.) was slowly distilled as described before. On working up the reaction product in the usual manner, the unsaturated cyano-ester distilled at 200-8°/4 mm., yield 31 g. (Found: N, 4·4. $C_{19}H_{23}O_4N$ requires N, 4·26 per cent).

α-Phenyl-δ-methyl-δ-carboxypimelic Acid (XIV).—The unsaturated cyano-ester (XII) (31 g.) in aqueous alcohol (120 c.c., 95%) was treated with a solution of potassium cyanide (13 g.) in water (70 c.c.). The product on cooling was further treated with hydrochloric acid (*d* 1·15, 16 c.c.) diluted with 11 c.c. of water in the same way as described before. After allowing the whole reaction mixture to stand for ½ hour at the ordinary temperature, it was acidified with 300 c.c. of dilute hydrochloric acid. The precipitated oil was extracted with ether. On removal of ether the crude residue, consisting of the dicyano-ester, was hydrolysed by refluxing with concentrated hydrochloric acid (300 c.c.) for 50 hours. Even when the mixture was hot, most of the tricarboxylic acid remained as an insoluble viscous gum at the bottom, but on cooling a small quantity of the tricarboxylic acid separated in the solid state from the clear supernatant solution. The latter was separated and crystallised from dilute alcohol, m.p. 169-71°. (Found : C, 61·4 ; H, 6·2 ; Equiv., 95. $C_{15}H_{18}O_6$ requires C, 61·2 ; H, 6·1 per cent. Equiv., 98).

Diethyl α-Phenyl-δ-methyl-δ-carbethoxypimelate.—The crude gummy acid, which separated in the above experiment from the hot liquid, was taken up in ether, the ethereal solution was dried with freshly ignited sodium sulphate The residue (18 g.), obtained on evaporation of the ether, was esterified by refluxing with absolute alcohol (200 c.c.) and sulphuric acid (d1·84, 28 c.c.) for 36 hours. The reaction mixture was worked up in the usual manner and the triethyl ester on distillation boiled at 202·4°/5 mm. (Found : C, 66·9 ; H, 7·9. $C_{21}H_{30}O_6$ requires C, 66·7 ; H, 7·9 per cent).

2 : 3-*Dicarbethoxy-3-methyl-6-phenylcyclohexanone* (IV, R=Ph ; R'= CO_2 Et)—The tricarboxylic ester (19 g.) in dry benzene (100 c.c.) was refluxed with sodium dust (2·3 g.) for 6 hours on the water-bath. The reaction mixture on cooling was worked up in the usual manner, the product distilled as a viscous oil (7 g.) at 195-97°/5 mm with some decomposition, It gives a deep violet colouration with alcoholic ferric chloride. From the analytical data it has been concluded that the above product consists mainly of the β-ketonic ester contaminated with a small quantity of the keto-ester (IV, R=Ph ; R'=H) formed by decomposition during distillation. (Found : C, 69·9, 70·5 ; H, 7·2, 7·6. $C_{19}H_{24}O_5$ requires C, 68·7; H, 7·2 per cent. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7 per cent).

3-*Methyl-3-carbethoxy-6-phenylcyclohexanone, Ethyl-1-keto-3-methyl-3-carbethoxy-6-phenylcyclohexane-2-acetate and Ethyl 1-keto-3-methyl-3-carbethoxy-6-phenylcyclohexane-2-propionate.*—For the condensation of the β-ketonic ester (IV, R=Ph : R'=CO_2Et) with ethyl bromoacetate and ethyl β-chloropropionate, experiments were carried out in the following manner. IV (R=Ph ; R'=CO_2 Et) (55 g.) was refluxed with sodium dust (6·7 g.) in dry benzene (150 c.c.) for 8-9 hours on the water-bath, the reaction mixture was cooled and treated with ice-cold dilute hydrochloric acid, the benzene layer separated, washed with sodium bicarbonate solution and water, dried and benzene removed, the crude product (35 g.) was then treated with sodium dust (2.4 g.) in benzene suspension and then ethyl bromoacetate (20 g.) was added to it and the whole was refluxed for 24 hours on the water-bath. Water was added to it after cooling and the layer was separated, washed with water, dried and benzene removed. The crude product was hydrolysed by boiling with concentrated hydrochloric acid (300 c.c.) for 30 hours. The acid mixture was cooled and the acidic products extracted with ether. The ethereal solution was dried and the gummy residue left on evaporation of ether was esterified by refluxing with absolute alcohol (100 c.c.) and

sulphuric acid (10 c.c.) for 24 hours, on a boiling water-bath. The ester mixtures were worked up in the usual manner and fractionated under reduced pressure, when 10 g. of 3-methyl-3-carbethoxy-6-phenyl*cyclo*hexanone, b. p. 182-87°/6 mm., was obtained. (Found : C, 73.5; H, 8.1 $C_{16}H_{20}O_3$ requires C, 73.8 ; H, 7.7 per cent).

The semicarbazone was crystallised from ethyl alcohol and melted at 175.5-176.5°. (Found· N, 13·7. $C_{17}H_{23}O_3N_3$ requires N, 13.3 per cent). About 6 g. of ethyl 1-keto-3-methyl-3-carbethoxy-6-phenyl*cyclo*hexane-2-acetate, b p. 180-86°/2.5 m.m., were also obtained. (Found : C, 69,6 ; H, 7.5 $C_{20}H_{26}O_5$ requires C, 69.36 ; H, 7.5 per cent).

In another experiment 7 g. of the substance, which mainly consisted of (IX, R = Ph ; R' = CO_2 Et) contaminated with (IV, R = Ph; R' = H) were treated with finely divided potassium (0·82 g.) suspended in xylene in the cold and left overnight when most of the potassium passed into solution. Ethyl β-chloropropionate (3 g.) was added and the solution refluxed for 24 hours. On working up in the usual manner and proceeding in a similar way with the crude product as before, the keto-ester (IV, R = Ph; R' = H) was obtained as a lower boiling fraction and a small quantity of ethyl 1-keto-3-methyl-carbethoxypheny-*cyclo*hexane-2-β-propionate distilled at 185-190°/1·6 mm. (Found : C, 70.3; H, 7.6. $C_{21}H_{28}O_5$ requires C, 70·0. H, 7.77 per cent).

Reformatsky's Reaction with Keto-ester (IV, R = Ph; R' = $CH_2 \cdot CO_2$ Et . The keto-ester (10·5 g) was refluxed with zinc wool (4 g.) and ethyl bromoacetate (7·6 g.) in dry toluene (20 c.c.) with the addition of a crystal of iodine for 5-6 hours, when the vigorous reaction which ensued at he start, completely subsided. The reaction mixture was decomposed with ice-cold dilute sulphuric acid, the toluene layer was separated and washed with sodium bicarbonate solution and water and then dried. Toluene was removed under diminished pressure and the residue fractionated, when about 2·5 g. of a viscous yellow oil were collected at 186-200°/1·8 mm. [Found : C, 68·9; H, 7.5 ; M.W. (by freezing point method), 410. $C_{24}H_{32}O_6$ requires C, 69·2; H, 7·7 per cent. M.W., 416)

Keto-deoxyoestric Acid (XVI).—The above compound (2 g.) was refluxed with an excess of red phosphorus and hydriodic acid (d 1·7) for a prolonged period. The reaction mixture was diluted and filtered and the filter paper was well washed with ether, which was added to the filtrate. The ethereal layer was separated, washed with water and dried

over sodium sulphate. On removal pf ether about 1 g. of an uncrystallisable resinous mass was left as a residue.

The crude product (o.8 g.) was heated with concentrated sulphuric acid (d 1·84; 4 c.c.) on a boiling water-bath for 10 minutes. The solution was cooled and crushed ice was added to it, when a heavy oil separated which was extracted with ether, the ethereal layer was washed with water, dried and ether removed. An oily residue, which was left behind, was treated with a concentrated aqueous solution of semicarbazide hydrochloride and sodium acetate and methyl alcohol when a small quantity of the semicarbazone separated as a reddish powder on standing. The product even after crystallisation from dilute methyl alcohol, was somewhat coloured, m.p. 165-75°. (Found : N, 10·4. $C_{19}H_{23}O_5N_3$ requires N, 11·2 per cent).

THE STABILITY AND STATE OF ASCORBIC ACID IN URINE.

BY SACHCHIDANANDA BANERJEE.

The stability of ascorbic acid in urine has been investigated in presence of different acids. The presence of combined ascorbic acid in urine is shown.

Recently vitamin C sub-nutrition has been associated with the etiology of various diseases. This vitamin C sub-nutrition is diagnosed by urine analysis. As the rate of excretion of ascorbic acid in urine is not uniform throughout the day and night, ascorbic acid content of 24 hours' urine should be determined. But ascorbic acid in urine is gradually lost on standing. Borsook *et al* (*J. Biol. Chem.*, 1937, **117**, 237) have shown that in an alkaline medium ascorbic acid may be oxidised to dehydroascorbic acid and 2:3-diketo-*l*-gulonic acid. The latter reaction being irreversible, only dehydroascorbic acid would be reduced to ascorbic acid when sulphuretted hydrogen is passed into the urine. It is, therefore, important to know under what conditions vitamin C in urine collected over 24 hours would be most stable. Although some work has been carried out on the subject, the position is by no means clear. As we also propose to investigate the state in which ascorbic acid is present in urine, it is necessary to know the factors concerned with the stability of vitamin C in urine in our conditions of experiment.

Freshly passed urine was treated separately with acetic acid, metaphosphoric acid, hydrochloric acid, sulphuric acid and diethyl dithiocarbamate. The last reagent was used in order to prevent any possible oxidation of vitamin C by means of traces of copper. The concentration of acids in urine was 5% by volume in each case ; the concentration of diethyl dithiocarbamate was 0·06 g. in 100 c.c. of urine. Samples of freshly voided urine were treated as above. Some samples were then titrated immediately with 2:6-dichlorophenol-indophenol (1 c.c. dye≡0·104 mg. of ascorbic acid) and others were kept overnight and titrated after 24 hours. The average results with the different treatments are shown in Table I.

TABLE I.

	1 C c. of the dye was decolorised by	
Urine kept with	Freshly voided urine.	Urine preserved for 24 hours.
Acetic acid	1·45 c.c.	6 70 c.c.
Metaphosphoric acid	,,	1·90
Hydrochloric ,,	,,	1·45
Sulphuric ,,	,,	1·45
Diethyl dithiocarbamate	,,	3·10

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It is clear from Table I that hydrochloric and sulphuric acids preserve the vitamin best. Metaphosphoric acid is next best, while acetic acid, which has been most commonly used for preservation, is the least effective. Diethyl dithiocarbamate is also largely ineffective. Acetic acid and metaphosphoric acid impart no colour to the urine but sulphuric acid and hydrochloric acid impart colour to the urine. Hydrochloric acid gives a deeper colour to the urine than sulphuric acid, so that sulphuric acid is considered to be the best preservative under our conditions of experiment.

In order to find how far this stability produced by sulphuric acid is specifically related to ascorbic acid, different samples of urine treated with sulphuric acid were subjected to treatment with ascorbic acid oxidase. Results are shown in Table II. The fact that figures in columns 3 and 5 are substantially in agreement shows that sulphuric acid has not produced any non-specific reducing substances *de novo*. On the other hand very substantial differences between values obtained before and after oxidase treatment indicate that titrations of urine without such treatment would lead to erroneous results.

TABLE II.

| | C.c. of urine required to reduce 0·5 c.c. of the dye | | | |
| | Urine (with H_2SO_4, 5%) freshly voided | | Urine (with H_2SO_4, 5%) after 24 hours. | |
Urine sample No.	Before oxidase action.	After oxidase action.	Before oxidase action.	After oxidase action.
1	2·40	7·35	2·40	7·40
2	1·25	5·60	1·25	5·55
3	0·75	3·50	0·75	3·60
4	1·30	3·46	1·30	3·50
5	1·50	5·80	1·50	5·70
6	2·15	5·00	2·15	5·00

In order to see whether ascorbic acid added to urine containing 5% sulphuric acid can be correctly estimated or not as a further test of the reliability of this method, 5 mg. of ascorbic acid were added to 100 c.c. of urine containing 5% sulphuric acid. Titrations were carried out immediately and after 24 hours. Table III shows that the added ascorbic acid could be correctly estimated, as the values obtained by immediate titration and by titration after 24 hours are identical.

TABLE III.

C.c. of urine required to reduce 1 c.c. of the dye

Urine sample No.	Immediate titration.	Titration after 24 hours.
1	1.35	1.35
2	1.25	1.25
3	0.80	0.80
4	1.00	1.00

The State of Ascorbic Acid in Urine.

Investigations from this laboratory have shown that certain plant foodstuffs contain ascorbic acid in a combined state (Guha and Pal, *Nature*, 1936, **137**, 946 ; Guha and Sen-Gupta, *ibid.*, 1938, **141**, 947 ; Sen-Gupta and Guha, *J. Indian Chem. Soc.*, 1939, **16**, 496). That urine also contains a part of ascorbic acid in a combined state was indicated by them (Guha and Sen-Gupta, *Nature*, 1938, **141**, 947) Scarborough and Stewart (*Biochem. J.*, 1937, **31**, 2231) have also made similar observations. In the present paper a more detailed study of the subject is presented, as it was important for us to know which method would give reliable values of the free, combined and dehydroascorbic acid of urine. This information was necessary in connection with researches undertaken in this laboratory on the rôle of vitamin C in the normal condition of the body and in infections.

All urine used was freshly passed. The titrations were carried out using 2 : 6-dichlorophenol-indophenol as indicator. A 50 c.c. portion of urine was immediately titrated. Another aliquot of 50 c.c. of urine was taken in a conical flask into which H_2S was passed for 20 minutes. Excess of H_2S was removed by a current of carbon dioxide. This was then titrated with the dye. Into another 50 c.c. of urine cold H_2S was passed for 5 minutes to chase out the air. The flask was then immersed in a bath of boiling water and H_2S was passed for 10 minutes. The flask was then placed in a beaker of cold water and H_2S was passed for 5 minutes, by which time the flask cooled. Excess of H_2S was removed by a current of carbon dioxide and the urine then titrated as before

Ascorbic acid oxidase was prepared from cucumber, approximately according to the method of Tauber *et al* (*J. Biol. Chem.*, 1935, **110**, 559). 660 G. of cucumber were chopped in a mincer and treated with 1800 c.c. of 30% alcohol. The mixture was shaken for 5 minutes and quickly filtered through glass wool, 1800 c.c. of acetone were added to the filtrate to precipitate the oxidase. The precipitate was quickly centrifuged off, dissolved in 240 c.c. of water, precipitated by 240 c.c. of acetone and centrifuged.

The precipitate was dried in a vacuum desiccator, and dissolved in 240 c c. of water and a drop or two of toluene was added. 1 C c. of this enzyme preparation could oxidise o·5 mg. of ascorbic acid. The stability of the preparation has been investigated by Sen-Gupta and Guha (*J. Indian Chem. Soc.*, 1939, **16**, 549). The activity of the enzyme was determined by the amount of ascorbic acid solution oxidised by the method previously described (Ghosh and Guha, *J. Indian Chem. Soc.*, 1937, **14**, 721). 5 C.c. of untreated urine, cold H_2S-treated urine and hot H_2S-treated urine were taken in three 50 c.c. flasks. The p_H was brought to 5·6 ·· 3 C.c. of the oxidase solution and 2 c.c. of *M*. acetate buffer (p_H 5·6) were added. These flasks were incubated at 37° for half an hour after which they were titrated. The difference in the titration values before and after oxidase treatment gives the true value of ascorbic acid. The results are shown in Table IV.

TABLE IV.

Mg. of indophenol reducing substances in 1 c.c of urine calculated as ascorbic acid.

Sample No.	Immediate direct titration.		Cold H_2S titration.		Hot H_2S titration.	
	Apparent ascorbic acid	True ascorbic acid.	Apparent ascorbic acid	True* ascorbic acid.	Apparent ascorbic acid.	True* ascorbic acid.
1	o·o866	o·o715	o·1038	0 0771	o·1600	o·o844
2	0 1223	o·o877	o·1600	o·1105	0 2080	o·1509
3	o·o385	o·o218	0 1300	o·o828	o·1890	0 1147
4	o·1040	0 0640	o·1320	o·o660	o·1400	o·1400
5	o·o217	0 0035	o·o397	o·ɔ194	ɔ·o643	0 0226
6	o·o288	o·o264	o·o399	o·o275	o·o495	0 0329
7	o·oo86	o·oo38	0 0152	o·oo40	0 0169	o·oo41
8	o·o252	o·o122	0 0346	o·o212	o·o371	o·o223

In order to investigate the nature of the non-specific reducing substances in the urine, the fresh urine and hot H_2S-treated urine were treated respectively with barium acetate, so that its final concentration in the urine was 5%. The filtrate was treated with concentrated H_2SO_4 to remove the excess of barium and the p_H was brought to about 3. The titrations were then carried out as usual. The results are shown in Table V.

* as determined by oxidase treatment.

TABLE. V.

Mg of indophenol reducing substance in 1 c.c. of urine calculated as ascorbic acid.

Sample No.:	Original as such	Original urine after		Hot H₂S-treated urine.	Hot H₂S-treated urine after	
		oxidase treatment.	Ba-acetate treatment.		oxidase action.	acetate treatment.
1	0'0260	0'0104	0'0144	0'0550	0'0160	0'0200
2	0 0192	0'0099	0'0140	0 0290	0'0100	0'0150
3	0'0081	0'0044	0'0052	0'0169	0'0129	0'0099
4	0'0081	0'0038	0'0057	0'0169	0 0041	0'0099
5	0'0288	0'0264	0'0273	0'0495	0'0329	0'0400

DISCUSSION.

These results indicate that urine contains besides ascorbic acid other substance or substances which decolourise 2 : 6 dichlorophenol-indophenol. After reduction with cold H_2S there is an increase of the dye-reducing substance. This increase is partly due to the increase in the ascorbic acid content as evidenced by treatment with ascorbic acid oxidase and partly due to other non-specific reducing substances. The higher ascorbic acid value is accounted for by the presence of dehydroascorbic acid which is reduced by sulphuretted hydrogen in the cold condition to ascorbic acid. Heating in presence of sulphuretted hydrogen gives rise to a dye-reducing value much higher than by reduction in the cold. Both ascorbic acid and some other reducing substances present are increased. Extra ascorbic acid liberated apparently comes from ascorbic acid present in the urine in a combined form, which as such has got no dye-reducing properties. It is interesting to note that along with combined ascorbic acid some non-specific reducing substance is also present in combined form which is also simultaneously split up by heating.

Results of treatment with barium acetate, which removes thiosulphate and some thiol bodies, indicate that this kind of non-specific reducing substances is present in ordinary urine and is also produced by treatment with hot sulphuretted hydrogen.

CONCLUSIONS.

Treatment with acetic, meta-phosphoric, hydrochloric, sulphuric acids and with diethyl dithiocarbamate shows that sulphuric acid is the

best preservative for vitamin C in urine. This has been confirmed also by treatment of the urine with ascorbic acid oxidase.

Treatment of urine with sulphuretted hydrogen in the cold and hot conditions shows that urine contains ascorbic acid, dehydroascorbic acid, combined ascorbic acid and non-specific reducing substances both in the free and combined states. This has been shown by treatment with ascorbic acid oxidase as well as with barium acetate.

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OBSERVATIONS ON THE ANTERIOR PITUITARY-LIKE GONADOTROPIC HORMONE FROM THE HUMAN URINE OF PREGNANCY. PART I.

By A. C. MAJUMDAR.

The anterior pituitary-like gonadotropic hormone from pregnancy urine has been concentrated. The most concentrated preparation contains nitrogen (6·89%), carbohydrate (6·68%) and tyrosin (2·20%) It gives negative Millon's, Molisch and Fehlings' tests but positive xanthreproteic and orcinol-sulphuric acid test. It is stable below p_H 5·6 at 10°. It is partially inactivated by H_2S and H_2O_2.

The presence of a sex-hormone in the urine of pregnancy, which is different from follicular and luteal hormones and resembles the hormone of the anterior lobe of the pituitary gland, which influences the gonads both in the male and in the female, was first indicated by Aschheim and Zondek (*Klin. Woch.*, 1928, **7**, 1401). It has been called the anterior pituitary-like gonadotropic hormone of pregnancy urine, as it appears to resemble but is not identical with the hormone of the anterior pituitary body itself. The hormone preparation from pregnancy urine has been extensively used in medical therapy. Its chemical isolation, however, has not yet been possible and until this is done many biochemical questions particularly those of interaction between the different sex-hormones will remain unexplored. This paper deals with attempts at the concentration of this substance with a view to its eventual isolation. Several workers (Van Dyke and Lawrence, *J. Pharmacol.*, 1931, **43**, 93 ; Dickens, *Biochem. J.*, 1930, **24**, 1507 ; Fishcher and Ertol, *Z. physiol. Chem.*, 1931, **202**, 83 ; Reiss and Haurowitz, *Z. exp. Med.*, 1929, **68**, 371 : Funk and Zeifirow, *Biochem. J.*, 1932, **26**, 619 ; Katzman and Doisy, *J. Biol. Chem.*, 1932, **98**, 739 ; Zondok *et al, Biochem. Z.*, 1933, **258**, 102) have also attempted to concentrate this hormone and their efforts have been attended with a partial measure of success.

Our method involves the separation of the active substance by the adsorption of the material on benzoic acid followed by the removal of benzoic acid by treatment with cold acetone as suggested by Funk and Zeifirow (*loc. cit.*) and Katzman and Doisy (*loc. cit.*).

EXPERIMENTAL.

Seven litres of human urine of late pregnancy were collected in a glass jar surrounded by ice and preserved at 0° for 36 hours. The p_H of the

cold urine was adjusted to 4·3 by means of glacial acetic acid. It was centri-
fuged and the clear supernatant liquid was transferred to a glass vessel
immersed in ice. While stirring it with a mechanical stirrer, 530 c.c. of
acetone saturated with benzoic acid (room temperature 30°) were gradually
added to the liquid in the vessel. The precipitated benzoic acid absorbate was
filtered under suction and thoroughly washed with 200 c.c. of a saturated
aqueous solution of benzoic acid. It was then treated with 530 c.c. of cold
acetone (10°), filtered and washed with another 100 c.c. of cold acetone.
It was dried overnight in a vacuum desiccator (10°) over $CaCl_2$ and
triturated with 50 c.c. of water in a glass mortar. The active material was
eluted by 0·05N-NaOH by adjusting the p_H to 9·6. In order to avoid the
destruction of the activity of the substance in alkaline medium the p_H
of the substance was quickly readjusted to 7·0 by means of acetic acid
The syrupy solution was centrifuged, the precipitate was twice washed with
water and the washings were added to the centrifugate. The solution was
made up to 75 c.c. and treated with 750 c.c. of cold acetone (10°.) Minute
particles of a white precipitate settled at the bottom when kept for 25 minutes
at 10°. This precipitate was separated and dried over $CaCl_2$ in a vacuum
desiccator. A brownish scale-like substance (0.6 g.) was obtained.

Biological Assay.

Immature female albino rats weighing between 30 g. and 42 g. were
taken for testing the active substance. The animals were kept on normal
diet consisting of milk, brown bread and whole wheat. A solution contain-
ing 0·24 mg. of the concentrated material per c.c. was kept in a cold store
(10°). A daily dose of 0·3 c.c. of this solution was injected intraperitonia-
lly into each animal. A group of 4 animals was treated with this
solution for 5 days. It was observed that the vagina of the four controls
remained closed whereas that of all the treated animals opened before the
5th day after the first dose was injected into the animals. On the 6th day
the vaginal smears of all the animals were tested. The serous smear of the
treated animals took 0·5% eosine stain. There were non-neucleated
cornified squamous cells associated with leucocytes and red blood cells.
The mucoid smear of the controls did not give the positive maturation test
in the vaginal smear. There was a distinct enlargement of the ovaries and
uteri of the treated animals as is observed from Table I given below.

Effect of the Change of p_H on the Biological Activity of the Substance.

A solution containing 0.24 mg. of the active material per c.c. was
adjusted to three different p_H values by means of diluted hydrochloric

acid and sodium hydroxide. The solutions were kept at 10°. The activity was tested as described above. The ovaries of all the animals as well as the uteri were separated and the mean weight of each group was taken. The results are given in Table I.

TABLE I.

p_H	No. of animals	Mean body wt. of the animals.	Mean wt. of the ovaries and uteri.	Mean weight of the ovaries & uteri per g. of the mean body wt.
3·6	4	35 g.	126 mg.	3·6 mg.
5·6	4	35	88	2·5
8·6	4	34	96	2·8
(untreated controls)	3	38	75	1·9

From Table I it appears that the substance is fairly stable within the range of p_H 3·6 to 8·6.

Electrodialysis.

A solution containing 3 mg. of the active extract per c.c. was divided into three portions and the p_H of the solutions was adjusted to three different values : (a) 3·6 (b) 6·6 and (c) 8·6 by means of glacial acetic acid and sodium hydroxide.

(1) To 10 c.c. of the solution (a) 5 c.c. of phosphate-citrate buffer of p_H 3·6 were added.

(2) To 10 c.c. of the solution (b) 5 c.c. of phosphate buffer of p_H 6·6 were added.

(3) To 10 c.c. of the sample (c) 5 c.c. of phosphate buffer of p_H 3·6 were added.

All the three samples (1), (2) and (3) were electrodialysed in a cold store (4°) for 4 hours at 220 volts and 9 milli amp. An agar-agar bridge of 2% agar-agar with 2% sodium chloride and parchment paper were used. In order to maintain a steady current of 9 milli amp. the concentration of the buffer of the side-chamber of the dialyser was different from that of the central chamber although other factors of the experiment were constant. For p_H 3·6, p_H 6·6 and p_H 8·6, the buffer for the side-chambers was diluted 20 times, 10 times, and 7 times respectively. Testing the solutions in the different compartments showed that the active material was not dialysable through parchment paper within the p_H range studied:

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Further Concentration of the Active Material.

In connection with the above experiments it was observed that the solution of the active substance gave a precipitate when the p_H was adjusted to 3·6 by means of glacial acetic acid. 10 C.c. of the solution containing 0·24 mg. of the active material per c.c. were, therefore, adjusted to p_H 3·6 by means of glacial acetic acid and the mixture centrifuged. The clear contrifugate (A) was found to be active. The precipitate was treated with 10 c.c. of water, and the p_H adjusted to 6·8 by means of sodium hydroxide. This was found to be inactive (Table II).

TABLE II.

Substance	Total solid material injected.	Number of animals.	Mean body weight.	Mean weight of the ovaries and uteri.	Mean wt. of the ovaries & uteri per g. of mean body wt
Centrifugate at p_H 3.6 (A)	0·096 mg.	3	35 g.	145 mg.	4·1 mg.
Precipitate from (A) dissolved at p_H 6.8	0·140	3	34	71	2·1
Untreated controls		3	39	86	2·2

Table II shows that none of the active material is precipitated by glacial acetic acid at p_H 3·6. It was also found that about 59% of the inactive solids were eliminated by this process.

When a concentrated syrupy solution of the extract containing 20 mg. of the crude substance was adjusted to p 3·6 by means of glacial acetic acid a precipitate, as stated above, was formed. This was centrifuged off and the clear liquid was treated with 10 times its volumes of cold acetone (12°). A white precipitate was obtained which was filtered under suction and dried in vacuum over $CaCl_2$ (10°). An amorphous white hygroscopic powder was obtained, which was about 41% of the original crude substance. This acetone-precipitated active material contained about 60% of the original active material.

Effect of H_2S and H_2O_2 on the Centrifugate (A) at p_H 3.6.

The samples of the contrifugate (A) at p_H 3·6 were treated separately with H_2S and H_2O_2.

(a) H_2S was passed for 5 minutes into 5 c.c. of the solution and then removed completely by CO_2.

(b) Three drops of 30% H_2O_2 were added to 5 c.c. of the solution.

(c) A sample of the solution was kept as a positive control.

These were biologically tested and the results are shown in Table III. The effect of the centrifugate was taken as 100 and of the treated fractions as percentages of this.

TABLE III.

Number of animals		Solution treated by	Activity.
3		Untreated active solution	100
3		H_2O_2	75
3		H_2S	67
3	(untreated controls)	—	0

Stability of the Centrifugate (A) at 10°.

The solid substance was found to remain active for a long time. But the whole of activity was lost within 8 days when the substance was kept without any buffer in an aqueous solution and the p_H of the solution was between 5·6 and 8·6 at 10°. The alteration of the p_H during the same time is shown in Table IV, which would indicate that the loss of activity from p_H 5·6 upwards is accompanied by a shift of p_H.

TABLE IV.

From p_H		to p_H.
3·6	...	3·6
5 6	...	5·4
7 2	...	6·2
8·6	...	6·6

Different Chemical Tests.

The active material obtained before treatment with glacial acetic acid did not give any positive Molisch, Millon's or Fehing's test, nor did it give any precipitate with phosphotungstic or trichloroacetic acid. It gave a precipitate readily with lead acetate, mercuric chloride and acetone. Definite xanthoproteic and orcinol-sulphuric acid tests were, however, obtained.

Analytical Results of the Purified Substance.

The purified material obtained by acetone precipitation was found to contain 6·89% of N, whereas the crude substance obtained by the simple adsorption of the active substance on benzoic acid contained 12·08% N. The purified material contained 6 68% of carbohydrate as estimated by the orcinol-sulphuric acid method of Sorensen and Haugaard (*Biochem Z.*, 1933, **260**, 619) as improved by Kondo and Muragama (*J. Agr. Chem. Soc., Japan* 1937, **13**, 473). The tyrosine content of the substance was determined by Wu's method using the phenol reagent and found to be 2·20%. It may be mentioned that the carbohydrate content of our preparation was comparable with the carbohydrate content (6.0%) of the gonadotropic preparation obtained from the anterior pituitary by Hartzman and Bens (*Nature*, 1938, **142**, 115) and it was considerably less than the value 19·0% found by the same authors (*loc. cit.*) for the substance obtained from pregnancy urine.

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THE PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD N-C-S. PART IX. THIOBENZAMIDE.

By Hans Krall and Vidya Sagar.

In continuation of the previous work on phenylthiocarbamides the decompositions of thiobenzamide have been studied (i) with hydrolytic agenes (ii) with nitrous acid under various conditions of p_H. The reaction with nitrous acid in the presence of weak ac d shows that thiobenzamide is 40% in the form of $C_6H_5CSNH_2$ in neutral solution; other decompositions are simple and show that this configuration is almost completely changed by acids and alkalis to the *iso*thioamide torm C_6H_5CSHNH.

The chemistry of phenylthiocarbamides has been investigated in these laboratories with a view to study their structure in solution under different conditions of p_H (*J. Indian Chem. Soc*, 1935, **12**, 627, 635, 639; 1937, **14**, 474, 478; 1938, **15**, 217, 221). The problem was attacked chiefly through two reactions *viz*. (i) the action of hydrolytic agents and (ii) the action of nitrous acid on these compounds. The decomposition varied according to the p_H of the solution. As in these cases the decompositions were complicated by the presence of two apparently similar nitrogen atoms, a simpler case of triad N-C-S in thiobenzamide has been studied in the present investigation.

In the presence of normal alkali thiobenzamide decomposes chiefy into benzonitrile and hydrogen sulphide (67%) according to the equation

$$C_6H_5CSNH_2 \longrightarrow C_6H_5CN + H_2S \qquad \ldots \text{(}i\text{)}$$

Traces of ammonia are also produced but this is due to a secondary decomposition (*vide* experimental).

With normal acid, benzoic acid, hydrogen sulphide and ammonia are produced thus

$$C_6H_5CSNH_2 \longrightarrow C_6H_5 \cdot COOH + H_2S + NH_3 \qquad \ldots \text{(}ii\text{)}$$

and this occurs to the extent of 10%. The change also occurs to some extent (2%) even in neutral solution.

The action of nitrous acid on thiobenzamide has also been studied in the presence of strong acid and using one equivalent of sodium nitrite, the gas phase is mostly nitric oxide (79%), a change typical of the thiocarbamides; the oxidation product is a neutral product (m.p. 90°) which

proves to be dibenzylazosulphime. (*Ber.*, 1892, **25**, 1578), obtained by Gabriel and Hofmann by the interaction of alcoholic solution of iodine and thiobenzamide Unchanged thiobenzamide still remains and if two molecular equivalents of nitrous acid are employed, the amount of the gas evolved is almost double with the same composition as above. The gas phase and the identity of the oxidation product show the change to be

$$C_6H_5C \overset{\parallel}{\underset{S}{}} NH_2 + 4HNO_2 = C_6H_5C \overset{N}{\underset{S \quad N}{}} CC_6H_5 + 4NO + 2H_2O + S \quad \dots \quad (iii)$$

(Dibenzylazosulphime)

In the presence of weak acid using one equivalent of sodium nitrite the gas phase is N (40%) and NO (60%); but there is evidence to show that the reaction giving nitrogen occurs first

$$C_6H_5CSNH_2 + HNO_2 = C_6H_5CSOH + N_2 + H_2O \qquad \dots \quad (iv)$$

Dibenzylsulphime is still formed but to a less extent.

The action of sodium nitrite in the presence of weak acid suggests that thiobenzamide is present in neutral solution only to the extent of 40% in the configuration $C_6H_5CSNH_2$, since the presence of a weak acid is not likely to disturb the configuration of the compound. This is supported by the hydrolytic decomposition. Acids and alkalis completely change the configuration to the form

$$C_6H_5C \overset{NH}{\underset{SH}{}}$$

which easily suffers desulphurisation and is easily oxidised.

Now it has been also found that the decrease in sulphide, observed in case of phenylthiocarbamide (*J. Indian Chem. Soc.*, 1935, **12**, 641) but not explained by the authors, is to be attributed to the oxidation of sulphide to thiosulphate and sulphite, in presence of air. It has been found that the percentage composition studied in the presence of hydrogen remains the same. Thus the decrease noted in the case of thiobenzamide may also be attributed to the same cause.

EXPERIMENTAL.

Hydrolytic Reactions.

Expt. 1. Decomposition of Thiobenzamide by Boiling with Aqueous Caustic Potash.—Thiobenzamide (6·85 g.) and one equivalent of normal

caustic potash (50 c.c.) were refluxed together for 1 hour in a 500 c.c. round.bottomed flask, traces of ammonia being evolved. The contents of the flask were cooled and then distilled in steam for 10 minutes. The distillate contained an oil (b.p. 191°) identified as benzonitrile by hydrolysis with 70% sulphuric acid to benzoic acid and ammonia. The residual alkaline liquor contained much sulphide and some unchanged thiobenzamide. In a similar experiment omitting steam distillation sulphide was estimated by titrating against standard ammoniacal zinc solution. (Found: H_2S, 67 per cent). Ammonia was found to be 3%, estimated by absorbing in Volhard's trap containing excess of standard acid. It was found that alkali sulphide slowly decreased if boiling was continued for a longer period. Now it has been also found that the decrease in sulphide, previously studied in case of phenylthiocarbamide but not then explained, is attributed to the oxidation of sulphide to thiosulphate and sulphite, in the presence of air. It has been found that the percentage of sulphide in four and eight hours remains 21% in the presence of hydrogen. Oxidation is excluded if the experiment is conducted throughout the period of boiling in presence of hydrogen (*J. Indian Chem. Soc.*, 1935, **12**, 641).

Expt. 2. Action of Cold Concentrated Alkali on Thiobenzamide.— Thiobenzamide (1 g.) and potassium hydroxide (3·66 g.) were added to water (7 c.c.), a solution resulting in the cold, an emulsion of benzonitrile being produced immediately but no ammonia; therefore ammonia formed in the last experiment is to be attributed to the secondary changes.

Expt. 3. Decomposition of Thiobenzamide by Boiling with Aqueous Hydrochloric Acid.—Thiobenzamide (6·85 g.) and one equivalent of normal hydrochloric acid (50 c.c.) were refluxed together for 1 hour. Hydrogen sulphide formed was absorbed in Volhard's trap containing normal caustic potash (15 c.c.) and sulphide was estimated by titrating against ammoniacal zinc solution as before. (Found: H_2S, 9·5 per cent) and ammonia (10%) (found by difference in the titre value of the acid before and after the hydrolysis). No benzonitrile could be detected in this case.

Expt. 4. Decomposition of Thiobenzamide by Boiling with Water.— Thiobenzamide (6·85 g.) and water (50 c.c.) were boiled for 1 hour under reflux condenser attached to a trap containing 3% basic lead acetate (15 c.c. . (Found: PbS, 0·2468 *i.e.*, H_2S, 2 per cent). The hydrolysed product contained benzoic acid and unchanged thiobenzamide. The reaction went in an analogous manner to that of acidic hydrolysis.

Action of Nitrous Acid on Thiobenzamide in the presence of a Strong Acid.

Expt. 5. In Molecular Proportion of 1 : 1 (gas phase).—Thiobenzamide

(0·0685 g.; 1/2 mg. molecule) was tapped into the cup of Lunge's nitro-meter. Sodium nitrite (0·5 c.c., 1/2 mg. molecular proportion) was added and the reaction started by the addition of 1 c.c. of 4 N-HCl. Gas evolved was 10·8 c.c. at 24° and 748 mm i.e., 9·4 c.c. at N.T.P. After the treatment with FeSO4 volume was 2. c c. at N.T.P. The composition was therefore NO, 77·8; N, 22·2 per cent.

Expt. 6. In Molecular Proportion of 2 : 1 in two stages (gas phase) — Expt. 1 was repeated and the evolved gas expelled from the nitrometer. Sodium nitrite (0·5 c.c. 1/2 mg., second molecular proportion) was added. The evolution of the gas was slower than with the first equivalent. Gas evolved was 8·5 c.c. at 21·5° and 748 mm. or 7·6 c.c. at N.T.P. (Found: N, 25·3; NO, 74·7 per cent).

Expt. 7. In Molecular Proportion of 2 : 1 in one stage (gas phase). — Expt. 6 was repeated except that sodium nitrite (1 c.c., 1 mg. molecular proportion) was added in one stage. Gas evolved was 19·5 c.c. at 23·5° and 747 mm. or 17·14 c.c. at N.T.P. (Found: N, 24·6; NO, 75·4 per cent).

Expt. 8. Action of Nitrous acid on Thiobenzamide (neglecting the gas phase). —Thiobenzamide (137 g., 1 mg. molecular proportion) was dissolved in 40 c.c. of dilute alcohol (1 : 1) and mixed with 4 N-HCl (20 c.c.), and when crystals just appeared the solution was treated drop by drop with sodium nitrite (10 c.c.). The reaction occurred with effervescence and evolution of nitric oxide. A pink solid was formed and the mother-liquor when treated with alkaline lead acetate gave a precipitate of lead sulphide showing that unchanged thiobenzamide was still present. The pink solid was extracted with hot alcohol and filtered from the resinous mass and the filtrate deposited silky needles (m.p. 90°), identical with dibenzylazosulphime (*Ber.*, 1892, **25**, 1578). (Found: N, 11·8; S, 13·4. Calc. for dibenzylazosulphime, $C_{14}H_{10}N_2S$: N, 11·8; S, 13·4 per cent). Mixed melting point with Hofmann's compound, prepared by the interaction of alcoholic solution of iodine and thiobenzamide, was also 90°. If two molecular proportions of sodium nitrite were used the amount of di-benzylazosulphime formed was larger and very little unchanged thiobenz-amide was left in the solution after the experiment.

Action of Nitrous Acid on Thiobenzamide in the presence of a Weak Acid.

Expt. 9. In Molecular Proportion 1 : 1 (gas phase).—The rest of the procedure was the same except that here 2N-acetic acid (1 c.c.) was added after the addition of sodium nitrite so that the configuration of thiobenzamide might not be disturbed and the reaction might start in the

least p_H at the very outset. The action began with effervescence but not so vigorously as was noted in the case of hydrochloric acid. Gas evolved was 8·5 c.c. at 21·5° and 747 mm. or 7·6 c.c. at N T.P. (Found: N, 38·1; NO, 61·9 per cent). If in the experiment the evolved gas was examined after 5 minutes of the start of the reaction the composition was found to be N, 50%; NO, 50% showing thereby that the normal reaction of nitrous acid on an amino group occurred first.

Expt. 10. *In Molecular Proportion* 1.1 (*neglecting the gas phase*).— Thiobenzamide (1·37 g.) was treated with sodium nitrite (10 c.c.) and 2N-acetic (20 c.c.) as was done in case of hydrochloric acid. The reaction was slow and nitric oxide was evolved. Some pink solid was formed and floated on the solution. The pink solid was proved to be dibenzylazosulphime as in the case of hydrochloric acid.

8

ON CHLORALAMIDES. THE REACTION OF POTASSIUM CYANIDE ON α-CHLOROCHLORAL-CHLORO-2-METHOXY- AND α-CHLOROCHLORAL-BROMO-2-METHOXYBENZ-AMIDES AND THE HYDROLYSIS OF THE RESULTING α-CYANO COMPOUNDS.

By (Late) N. W. Hirwe and K. N. Rana.

α-Chlorochloral-chloro-2-methoxy- and α-chlorochloral-bromo-2-methoxybenzamides have been reacted with potassium cyanide to obtain α-cyano compounds of the type R·CO·NH·C(CN) : CCl₂. The nitriles have been hydrolysed with concentrated hydrochloric acid to the corresponding carboxylic acids which have formed metallic salts.

To extend the authors' previous investigations (*J. Indian Chem. Soc*, 1939, **16**, 677), the reaction of potassium cyanide has been tried on α-chloro-chloral-chloro-2-methoxy- and α-chlorochloral-bromo-2-methoxybenzamides R·CO·NH·CH(Cl)·CCl₃. The α-chlorine atom, being very reactive, better regulates the cyanide reaction than does the α-hydroxyl group, which as in chloral-acetamide and choral-benzamide, leads to complex substances of unknown constitution (Schiff and Speciale, *Gazzetta*, 1879, **9**, 335). By using an excess of potassium cyanide in dry acetone medium, α-cyano compounds have been isolated, which, however, are not the simple substitution products R·CO·NH·CH(CN)·CCl₃. It is found that potassium cyanide, besides substituting the α-chlorine atom, simultaneously removes a molecule of hydrogen chloride from the chloralamide group, giving rise to a ββ-dichloro -α-cyanovinyl derivative R·CO·NH·C(CN): CCl₂.

The spontaneous formation of unsaturation explains the need for the excess of potassium cyanide in the reaction. Chloral condensation compounds, R·CH(OH)·CCl₃, have long been known to yield dichlorovinyl derivatives by the action of alcoholic potash (*cf.* Goldschmidt, *Ber.*, 1873, **6**, 985), potassium cyanide here also acting like alkali.

The nitriles have been hydrolysed with concentrated hydrochloric acid to the corresponding carboxylic acids, R·CO·NH·C(COOH): CCl₂.

The yield of cyano compounds is rather poor (*ca* 39%), but their conversion into acids is quantitative. The acids are comparatively unstable and tend to decompose on melting (or heating with alkalis) with evolution of gas.

Although the above compounds are unsaturated, they do not add bromine due to the resisting polar effects of the adjacent radicals (*cf.* Hugo and Bauer, *Ber.*, 1904, **37**, 3317; Ley, *ibid.*, 1917, **50**, 243).

Hirwe and Deshpande (*private comunication*) have obtained analogous, unsaturated products, while studying the reaction of potassium cyanide on α-chlorochloral-tolylamides.

EXPERIMENTAL.

Potassium Cyanide Reaction.—Potassium cyanide (5 g) was added to a dry acetone solution of the freshly prepared α-chlorochloralamide (5 g.) in a bottle fitted with a spring stopper, with cooling and then the mixture was mechanically shaken for about $\frac{1}{2}$ hour, during which period a rapid colour change (usually from pinkish to rusty-red to brown) was observed. Shortly after this change of colour ceased the reaction mixture was poured into ice-water, when the α-cyano compound was precipitated.

Hydrolysis of the α-Cyano Compound.—The α-cyano compound (2 g.) and concentrated hydrochloric acid (50 c.c) were mixed together in a tube and heated under reflux on a steam-bath for about 2 hours, the mixture being well shaken from time to time. The solid, without going into solution, slowly changed into a flocculent mass. It was filtered off afer cooling, washed and then dissolved in a solution of sodium carbonate and filtered. The carboxylic acid was obtained by acidification of the solution with dilute hydrochloric acid.

The sodium salt of the acid was prepared in acetone solution by neutralisation ; other salts were prepared by double decomposition of the alkali or ammonium salt. The compounds described below gave no ferric reaction.

ββ-Dichloro-α-cyanovinyl -5-chloro-2-methoxybenzamide, prepared from α-chlorochloral-5-chloro-2-methoxybenzamide, is soluble readily in methanol, alcohol, acetone, glacial acetic acid and sparingly in chloroform and benzene. It crystallised from acetone in long, shining needles, m.p. 171-72°, yield 2 g. (Found: C, 43.35; H, 2·20; N, 9·0 ; Cl, 35·0. $C_{11}H_7O_2N_2Cl_3$ requires C, 43·21, ; H, 2·29 ; N, 9·17 ; Cl, 34·86 per cent).

ββ-Dichloro-α-carboxyvinyl-5-chloro-2-methoxybenzamide, prepared from ββ-dichloro-α-cyanovinyl-5-chloro-2-methoxybenzamide, is soluble readily in methanol, alcohol, acetone and sparingly in glacial acetic acid. It crystallised from acetone in white, shining needles m.p. 199-200° (decomp.) It turned pinkish on long standing. (Found : N, 4.17 ; Cl, 32·73; Equiv., 325·7. $C_{11}H_8O_4NCl_3$ requires N, 4 31; Cl, 32·83 per cent. Equiv., 324·5).

The *sodium salt* crystallised from water in pinkish needles. (Found: Na, 6·89. $C_{11}H_7O_4NCl_3Na$ requires Na, 6·64 per cent).

The *barium salt* crystallised from water in white needles which became pinkish on standing. [Found: Ba, 17.0; H_2O, 4·51. $(C_{11}H_7O_4NCl_3)_2Ba$, $2H_2O$ requires Ba, 16·75; H_2O, 4·39 per cent].

ββ-Dichloro-α-cyanovinyl-3:5-dichloro-2-methoxybenzamide was prepared from α-chlorochloral-3:5-dichloro-2-methoxybenzamide. It is soluble in methanol, alcohol, acetone and glacial acetic acid and crystallises from acetone in long, shining needles, m.p. 172-73°, yield 1·8 g. (Found: N,8·93; Cl, 42·04 $C_{11}H_6O_2N_2Cl_4$ requires N, 8·42; Cl, 41·77 per cent).

ββ-Dichloro-α-carboxyvinyl-3:5-dichloro-2-methoxybenzamide, prepared from ββ-dichloro-α-cyanovinyl-3:5-dichloro-2-methoxybenzamide, crystallised from acetone in long, shining needles, m.p. 202-3° (decomp.). (Found: Cl 39.33; Equiv , 358·1. $C_{11}H_7O_4NCl_4$ requires Cl, 39·56 per cent. Equiv. 358·9).

The *sodium salt* crystallised from water in pinkish needles. (Found: Na, 5·40; H_2O, 4.31. $C_{11}H_6O_4NCl_4$ Na, H_2O requirs Na, 5·76; H_2O, 4·5 per cent).

The *barium salt* crystallised from water in greenish yellow, thick plates. [Found: Ba, 15·19, 15·16. $(C_{11}H_6O_4NCl_4)_2Ba$, $4H_2O$ requires Ba, 14·85 per cent].

ββ-Dichloro-α-cyanovinyl-5-bromo-2-methoxybenzamide, prepared from α-chlorochloral-5-bromo-2-methoxybenzamide, crystallised from acetone in long shining needles, m.p. 177-78°, yield 2 g. (Found: N, 8·02; Halogen, 42·99. $C_{11}H_7O_2N_2Cl_2$ Br requires N, 8·0; Halogen, 43·09 per cent).

ββ-Dichloro-α-carboxyvinyl-5-bromo-2-methoxybenzamide, prepared from ββ-dichloro-α-cyanovinyl-5-bromo-2-methoxybenzamide, crystallised from acetone in shining needles, m.p. 203-4° (decomp). (Found: N, 3·70; Halogen, 40·82; Equiv., 368.5. $C_{11}H_6O_4NCl_2Br$ requires N, 3·79; Halogen, 40·87 per cent. Equiv., 368.9).

The *sodium salt* crystallised from water in needles. (Found: Na, 5·54. $C_{11}H_7O_4NCl_2BrNa$ requires Na, 5·88 per cent).

The *calcium salt* crystallised from water in plates. [Found: Ca, 5·10, 4.98. $(C_{11}H_7O_4NCl_2Br)_2Ca,2H_2O$ requires Ca, 4·93 per cent].

ββ-Dichloro-α-cyanovinyl-3:5-dibromo-2-methoxybenzamide was prepared from α·chlorochloral-3:5-dibromo-2-methoxybenzamide. It crystallised from acetone in long shining needles, m.p. 220-21° (decomp.), yield 2 g. (Found: N, 6·62; Halogen, 54·00. $C_{11}H_6O_2N_2Cl_2Br_2$ requires N, 6·53; Halogen, 53·83 per cent).

ββ-Dichloro-α-carboxyvinyl-3:5-dibromo-2-methoxybenzamide was prepared from *ββ*-dichloro-α-cyanovinyl-3:5-dibromo-2-methoxybenzamide. It crystallised from acetone in shining needles, m p. 217-18° (decomp.) It turned brownish on standing. (Found: Halogen, 51·36; Equiv., 447·3. $C_{11}H_7O_4NCl_2Br_2$ requires Halogen, 51·53 per cent. Equiv., 447.8).

The *sodium salt* crystallised from water in needles. (Found · Na, 4·38; H_2O, 7·40. $C_{11}H_6O_4NCl_2Br_2Na$, $2H_2O$ requires Na, 4·54; H_2O, 7·11 per cent).

The *barium salt* crystallised from water in plates. [Found: Ba, 12 92, 12 94. $(C_{11}H_6O_4NCl_2Br_2)_2Ba$, $3H_2O$ requires Ba, 12·66 per cent].

Our best thanks are due to Prof. R. C. Shah for his kind interest in this investigation.

CYANOCAMPHORANILIC ACIDS AND THEIR ROTATORY POWERS.

By Mahan Singh and Arjan Singh.

3'-and 4'-cyanocamphoranilic acids have been prepared and their rotatory powers determined. The position of CN group in the sequence of substituent groups is anomalous: It should be in the proximity of COOH group, but actually it falls with the halogens.

Rule and co-workers (*J. Chem. Soc.*, 1924, 1121 *et seq.*), have shown that the polar effect of a substituent group is manifest in optical activity. The order in which the substituents are arranged is identical with the order obtained from the dipole moment. This series such as NO_2, COOH, CN, Halogens, H, Me, NMe_2, which is deduced from the dipole moments, represents a gradual transition from strongly electronegative groups through hydrogen to those increasingly electropositive in character.

In previous papers (*J. Chem. Soc.*, 1925, 1967 ; 1927, 1996 *et seq.*, the following values were obtained for 4'-camphoranilic acids in methyl alcohol.

	COOH.	C_2H_5.	Cl.	OEt.	Me.	OMe.	Br.	I.
$[\alpha]_D$	255	59·0	58·8	56·3	56	53·3	51·3	44·16

We should expect that substitution of CN group in camphoranilic acid will increase the rotation of the parent compound. 4'-Cyanocamphoranilic acid, now prepared, has $[\alpha]_D$, 58·0 (methyl alcohol). The position of this group is, therefore, anomalous in the sequence of substituent groups; it should be in the proximity of COOH group.

3'-Cyanocamphoranilic acid, as expected, has smaller rotatory power than the corresponding 4'-isomeride in all the solvents tried.

Experimental.

Camphoric anhydride and cyanoaniline in molecular proportions were heated with a little fused sodium acetate for 3 to 4 hours in an oil-bath at 120-30° and the product extracted with alcohol. At a slightly higher temperature the yield diminished.

4'-Cyanocamphoranilic acid was extracted with alcohol (animal charcoal), and precipitated by the addition of water and crystallised from dilute

alcohol as a yellowish powder, m.p. 140°. (Found : N, 8·97 ; Equiv., 304. $C_{17}H_{20}O_3N_2$ requires N, 9·3 per cent. Equiv., 300).

3'-Cyanocamphoranilic acid, isolated in a similar way, was extracted with a dilute solution of sodium hydroxide or ammonium hydroxide and the product reprecipitated by the addition of dilute acetic acid or hydrochloric acid, the process being repeated till the m.p. rose to 108-10°. (Found : N, 8·5, 8·7 ; Equiv., 318. $C_{17}H_{20}O_3N_2,H_2O$ requires N, 8·8 per cent Equiv., 318).

Rotations of Cyanocamphoranilic Acids.

[The readings were taken in 2 dcm. tube]

Solvent.	Conc. g./25 c.c.	α_D.	$[\alpha]_D$.	Conc. g /25 c.c.	α_D.	$[\alpha]_D$
	3'-Cyanocamphoranilic acid.			4'-Cyanocamphoranilic acid.		
MeOH	0·20 g.	0·78°	48·4°	0·25°	1·16°	58·0
EtOH	0·20	0·62	38·8	0 25	1·03	51·5
Me₂CO	0·20	0·60	37·5	0·25	0·99	49 5
MeEtCO	0·20	0·47	29 3	0·25	0 80	40·4

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KOSTANECKI-ROBINSON REACTION. PART II. PROPIONYL-ATION AND BUTYRYLATION OF ORCACETOPHENONE AND ITS MONOMETHYL ETHER.

BY S. M. SETHNA AND R. C. SHAH.

In continuation of the work described in Part I orcacetophenone has been propionyl-ated and butyrylated. The condensation products on treatment with concentrated sul-phuric acid give 7-hydroxy-3 : 5-dimethyl-4-propionomethylcoumarin and 7-hydroxy-3-ethyl-4-butyromethyl-5-methylcoumarin respectively. These on treatment with alkali give 7-hydroxy-3 : 4 : 5-trimethylcoumarin and 7-hydroxy-3-ethyl-4 : 5-dimethylcoumarin respectively. 7-Hydroxy-2-ethyl-5-methylchromone and 7-hydroxy-2-propyl-5-methyl-chromone, required for comparison, have been synthesised from the β-diketones obtained by the condensation of orcacetophenone dimethyl ether with ethyl propionate and ethyl butyrate respectively.

Resacetophenone on Kostanecki acetylation gives a chromone (Kosta-necki and Rozycki, *Ber.*, 1901, **34**, 102). A similar acetylation of orcaceto-phenone and its monomethyl ether gave 7-acetoxy-4-acetomethyl-5-methyl-coumarin and, 7-methoxy-4-acetomethyl-5-methylcoumarin respectively. These on deacetylation gave 7-hydroxy-4 : 5-dimethylcoumarin and 7-methoxy-4 : 5-dimethylcoumarin respectively, as described in the previous part (Sethna and Shah, *J. Indian Chem. Soc.*, 1940, **17**, 239). The forma-tion of the 4-substituted *C*-acylcoumarins in Kostanecki acetylation has been observed for the first time in the above work. In view of these interesting results the work has been extended to the propionylation and butyrylation of orcacetophenone and its monomethyl ether.

Orcacetophenone on heating with sodium propionate and propionic anhydride yields a brown viscous mass. which cannot be either distilled or crystallised and so is directly treated with concentrated sulphuric acid for the hydrolysis of the O-propionyl group, when a product $C_{15}H_{16}O_4$ (A) is ob-tained which gives the acetyl derivative, methyl ether and 2 : 4-dinitro-phenylhydrazone. The product (A) on treatment with alkali gives (B) $C_{12}H_{12}O_3$, which is found to be not identical on direct comparison with 7-hydroxy-2-ethyl-5-methylchromone (III, $R = C_2H_5$) synthesised for the purpose. The structure of 7-hydroxy-3 : 4 : 5-trimethylcoumarin (I, $R = H$) has, therefore, been assigned to (B). The molecular formula of (A) differs from (B) by C_3H_4O which suggests the presence of a propionyl group. This group must be in the pyrone ring as it is easily split off by alkali and also because the product (A) does not give a ferric chloride colouration. The

structure of 7-hydroxy-3 : 5-dimethyl-4-propionomethylcoumarin (I, R = COC_2H_5) has been, therefore, assigned to (A) by analogy with the results obtained in the acetylation of orcacetophenone.

The monomethyl ether of orcacetophenone gives on similar propionyl-ation 7-methoxy-3 : 5-dimethyl-4-propionomethylcoumarin, identical with the methyl ether of (I, R = COC_2H_5).

An attempt has been made in this connection to synthesise 7-hydroxy-3 : 4 : 5-trimethylcoumarin through the Pechmann condensation of p-orsel-linic acid with ethyl α-methyl-acetoacetate. It has, however, been found that under the usual conditions of the reaction neither p-orsellinic acid nor methyl p-orsellinate condenses with ethyl α methyl-acetoacetate. Under more drastic conditions, a very small quantity of an acid is obtained which is found to be the same as the acid obtained on heating p-orsellinic acid alone with concentrated sulphuric acid under the above conditions of reaction. The acid is probably obtained by the condensation of two mole-cules of p-orsellinic acid and may have the structure (IV, R = COOH) of a diphenyl methyloid derivative, the product obtained on decarboxylation having the structure (IV, R = H).

Orcacetophenone on butyrylation gives a brown viscous product which cannot be purified and so is treated directly with concentrated sulphuric acid, when a product is obtained which is supposed to be 7-hydroxy-3-ethyl-4-butyromethyl-5-methylcoumarin (II, R = COC_3H_7) by analogy with the previous work. This on treatment with alkali gives 7-hydroxy-3-ethyl-4 : 5-dimethylcoumarin (II, R = H), which is found to be not identical on direct comparison with 7-hydroxy-2-propyl-5-methylchromone (III, R = C_3H_7).

The monomethyl ether of orcacetophenone on butyrylation gives brown viscous product which can neither be distilled nor crystallised.

Propionylation and butyrylation of monoethyl ether of resacetophenone gives a mixture of chromones and coumarins, the yield of the latter being greater than that of the former (Heilbron, Hey and Lythgoe, *J. Chem. Soc.*, 1934, 1581; 1936, 297). In the propionylation and butyrylation of orcaceto-phenone we have not been able to isolate any chromones. As in the acetyl-ation of orcacetophenone, 4-substituted C-acylcoumarins have been obtained. The 6-methyl group in orcacetophenone, therefore, seems to have a profound influence on the course of the Kostanecki reaction and the effect of this group may be steric.

The chromones required in this work for comparison have been pre-pared by the condensation of orcacetophenone dimethyl ether with ethyl propionate and ethyl butyrate respectively. The β-diketones are treated

with cold hydrobromic acid solution when methoxy chromones are obtained. These on heating with hydriodic acid give 7-hydroxy-2-ethyl-5-methyl-chromone (III, $R=C_2H_5$) and 7-hydroxy-2-propyl-5-methylchromone (III, $R=C_3H_7$) respectively.

Me $C\cdot CH_2R$
(I)

Me $C\cdot CH_2R$
(II)

Me   CO
(III)

· Me
(IV)

E X P E R I M E N T A L.

Propionylation of Orcacetophenone :   *7-Hydroxy-3:5-dimethyl-4-pro-pionomethylcoumarin* (I, $R=COC_2H_5$).—Orcacetophenone (10 g.), prepared by Hoesch's method (*Ber.*, 1915, 48, 1127) was refluxed with sodium propionate (30 g.) and propionic anhydride (100 c.c.) in an oil-bath at 180-190° for 9 hours. The excess of propionic anhydride was distilled over and the reaction mixture added to water. Dark brown viscous oil separated which did not solidify even on keeping for 3 to 4 days in a frigidaire. It was taken up in ether and the ether extract was thoroughly washed with sodium bicarbonate solution. The residue from ether extract, a dark brown viscous oil, could not be either distilled at reduced pressure or crystallised and so was treated with concentrated sulphuric acid (15 c.c.) and kept for 4 hours. The reaction mixture was then added to ice-cold water, when pale greenish yellow solid separated which was crystallised from rectified spirit in pale yellow tiny silky needles (4·5 g.), m.p. 207-9°. The product gave no fluorescence with concentrated sulphuric acid or caustic alkalis and showed no colouration with alcoholic ferric chloride. (Found : C, 68·9; H, 6·2. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2 per cent)

The acetyl derivative, prepared as usual with sodium acetate and acetic anhydride, was crystallised from rectified spirit in tiny shining needles, m.p. 111-13°. (Found : C, 67·4 ; H, 5·8. $C_{17}H_{18}O_5$ requires C, 67·5 ; H, 6·0 per cent).

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7-Methoxy-3:5-dimethyl-4-propionomethylcoumarin,   prepared   with potassium carbonate and methyl iodide as usual, was crystallised from rectified spirit in faint greenish needles, m.p. 75-77°. (Found : C, 70·1 ; H, 6·6. $C_{16}H_{18}O_4$ requires C, 70·1 ; H, 6·6 per cent).

The 2:4-dinitrophenylhydrazone, prepared as usual, was crystallised from alcohol-acetic acid mixture in yellow needles, m.p. 255-56° (decomp.). (Found : N, 12·1. $C_{21}H_{20}O_7N_4$ requires N, 12·7 per cent).

7-Hydroxy-3·4:5-trimethylcoumarin (I, R = H).—The product (I, R = COC_2H_5) (3 g.) was shaken up with sodium hydroxide (6%, 40 c.c.) and kept for 3 hours. The reaction mixture was then acidified with concentrated hydrochloric acid, when a pasty product came down which solidified on keeping in a frigidaire overnight. It was crystallised from rectified spirit and finally from 50% acetic acid in small slender needles (1 g.), m.p. 195-97°, mixed m.p. with 7-hydroxy-2-ethyl-5 methylchromone was depressed by 30°. The product gave bluish fluorescence with concentrated sulphuric acid and with caustic alkalis. (Found : C, 70·3; H, 6·0. $C_{12}H_{12}O_3$ requires C, 70·6 ; H, 5·9 per cent).

The *methyl ether,* prepared as usual by potassium carbonate-methyl iodide method, was crystallised from dilute alcohol in prisms, m.p. 90-92°. (Found : C, 70·7 ; H, 6·4. $C_{13}H_{14}O_3$ requires C, 71·6 ; H, 6·4 per cent).

Propionylation of Orcacetophenone Monomethyl Ether.—Orcacetophenone monomethyl ether (2 g.), prepared from orcacetophenone, dimethyl sulphate and alkali (Hoesch, *loc. cit.*), was refluxed with sodium propionate (6 g.) and propionic anhydride (20 c.c.) for 8 hours at 180-90°. The brown viscous mass, obtained as residue from ether extract, on working up as above was dissolved in rectified spirit and kept in a frigidaire when tiny faint yellow needles separated (0·4 g.), m.p. 74-76° (mixed m.p. with 7-methoxy-3:5-dimethyl-4-propionomethylcoumarin described above).

(2′:4′-Dimethoxy-6′-methyl)-benzoylpropionylmethane.—Dimethyl ether of orcacetophenone (6 g.), prepared from orcacetophenone, dimethyl sulphate and sodium hydroxide (Tambor, *Ber.,* 1908, 41, 794) and ethyl propionate (13 g., approximately 4 mol.) were added to pulverised sodium (1·5 g., approx. 2 mol.), the whole being cooled externally by cold water. After the initial vigorous reaction had subsided the reaction mixture was heated in an oil-bath at 115-20° for 1½ hours. On cooling, water was added to decompose the excess of sodium and the mixture was extracted with ether to remove the excess of ethyl propionate and the unreacted dimethyl ether of orcaceto-

phenone. The alkaline solution, on acidification with dilute acetic acid, gave an oil. This was taken up in ether, the ether extract was washed with sodium bicarbonate solution and dried The oil, obtained on evaporation of ether, was distilled under reduced pressure and the fraction which distilled over at 185-90°/2-4 mm. (4 g.) was collected. It gave deep reddish violet colouration with alcoholic ferric chloride. (Found : C, 67·2 ; H, 7·2. $C_{14}H_{18}O_4$ requires C, 67·2 ; H, 7·2 per cent).

7-Methoxy-2-ethyl-5-methylchromone.—The above β-diketone (2 g.) was kept for 24 hours with hydrobromic acid solution (d 1·78, 5 c.c.) and then poured into water. The brown solid, which separated, was treated with dilute sodium hydroxide to remove demethylated chromone if any. The portion insoluble in alkali was crystallised from rectified spirit in long slender needles (o 7 g.), m.p. 130-32°. (Found : C, 71·3 ; H, 6·3. $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4 per cent).

7-Hydroxy-2-ethyl-5 methylchromone (III, R=C_2H_5).—The above methyl ether (o·3 g.) was dissolved in acetic anhydride (3 c c.) and refluxed in an oil-bath at 130-140° for 2 hours with hydriodic acid solution (d 1·7, 5 c.c.). The product, obtained on adding the reaction mixture to sodium bisulphite solution, was treated with sodium hydroxide. The portion soluble in alkali came down on acidification with hydrochloric acid and was crystallised from rectified spirit in slender shining needles (o·15 g.), m.p. 195-97°. It gives blue fluorescence with concentrated sulphuric acid. (Found : C, 70·3 ; H, 5·9. $C_{12}H_{12}O_3$ requires C, 70·6, H, 5·9 per cent).

Attempted Pechmann Condensation of Methyl p-Orsellinate and p-Orsellinic Acid with Ethyl α-Methylacetoacetate.

(*i*) Methyl *p*-orsellinate (1 g.), prepared from *p*-orsellinic acid and diazomethane (Herzig, *Monatsh*, 1903, **24**, 894), ethyl α-methylacetoaceta e (1 g.) and sulphuric acid (80% , 10 c.c.) were kept for 40 hours. On working up as usual the product was found to be only *p*-orsellinic acid.

(*ii*) *p*-Orsellinic acid (5 g.), ethyl α-methylacetoacetate (4·5 g.) and concentrated sulphuric acid (30 c.c.) were kept overnight and next day the reaction mixture was heated at 60-70° for 4 hours. *p*-Orsellinic ac d was obtained back on working up the reaction mixture as usual.

(*iii*) The above reaction mixture (*ii*) was heated on a water-bath at 60-70° for 16 hours and poured into water. The product obtained was filtered, washed with water and treated with sodium bicarbonate solution when the whole of it went into solution. The product, obtained on acidi-

fication, was crystallised from rectified spirit in tiny pale greenish needles
(0·3 g.), m.p. 235-37° (efferv.). [Found: C, 63·9; H, 4·7. $C_{16}H_{12}O_6$
(IV, R=COOH) requires C, 64·0 ; H, 4·0 per cent). It gave greenish blue
colouration with alcoholic ferric chloride and intense greenish fluorescence
with alkali. The above product was heated for 5 minutes at 240-50° in an
oil-bath till the effervescence ceased, when a solid was obtained which was
crystallised from alcohol in tiny pale yellow needles, m.p. 265-67°.
[Found : C, 70·6; H, 5·5. $C_{15}H_{12}O_4$ (IV, R=H) requires C, 70·3 ;
H, 4·7 per cent]. The product gave pale bluish green colouration with
alcoholic ferric chloride and an intense greenish fluorescence with alkali.

Heating p-Orsellinic Acid with Concentrated Sulphuric Acid.—*p*-Orsellinic
acid (3 g.) was heated with concentrated sulphuric acid (25 c.c.) for 16
hours at 60-70°. The product, obtained on adding the reaction mixture
to water, was crystallised from rectified spirit in tiny yellow needles (0·2 g.),
m.p. 235-37° (efferv.), mixed m.p. with the acid obtained in (*iii*) above was ·
the same.

*Butyrylation of Orcacetophenone : 7-Hydroxy- 3-ethyl- 4-butyromethyl-
5-methylcoumarin* (II, R=COC_3H_7).—Orcacetophenone (10 g.), sodium
butyrate (30 g.) and butyric anhydride (100 c.c.) were refluxed in an oil-
bath at 180-90° for 8 hours, and the reaction mixture was added to water.
Excess of sodium bicarbonate solution was added and the whole kept in
a frigidaire. The brown viscous oil, which separated, did not solidify and so
was taken up in ether. The ether extract was washed with sodium bi-
carbonate solution. The brown viscous oil, obtained from the ether extract,
could neither be distilled nor crystallised out and hence was directly
treated with concentrated sulphuric acid (20 c.c) and kept for about 2
hours. The yellowish solid, obtained on pouring the reaction mixture into
cold water, was crystallised from rectified spirit (charcoal) in pale yellow
silky needles (6 g.), m.p. 155-56°. (Found : C, 70·6 ; H, 6·8. $C_{17}H_{20}O_4$
requires C, 70·8 ; H, 6·9 per cent).

The product gave no fluorescence with concentrated sulphuric acid or
with caustic alkalis and gave no colouration with alcoholic ferric chloride.

The *acetyl derivative*, prepared as usual with sodium acetate and acetic
anhydride, was crystallised from rectified spirit in needles, m.p. 79-80°.
(Found : C, 69·2 ; H, 6·7. $C_{19}H_{22}O_5$ requires C, 69·1 ; H, 6·7 per cent).

The *methyl ether*, prepared as usual by the potassium carbonate-methyl
iodide method, was crystallised from alcohol in tiny yellow needles, m.p.

51-54°. (Found: C, 71·4; H, 7·4. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3 per cent).

The 2 : 4- *dinitrophenylhydrazone*, prepared as usual, was crystallised from rectified spirit in tiny yellow needles, m.p. 253·54° (decomp.). (Found : N, 11·5. $C_{23}H_{24}O_7N_4$ requires N, 12·0 per cent).

7-Hydroxy- 3-ethyl- 4 : 5-dimethylcoumarin (II, R=H) —The condensation product (II, R = COC_3H_7) was treated with sodium hydroxide (10%, 40 c c.) and kept for 3 hours. The product, obtained on acidification, was crystallised from rectified spirit in clusters of white tiny needles (2 g.), m.p. 170-72°. Mixed m.p. with 7-hydroxy-2-propyl-5-methylchromone was depressed by 30°. (Found: C, 71·4; H, 6·4. $C_{13}H_{14}O_3$ requires C, 71·6 ; H, 6·4 per cent). The product gave bluish fluorescence with concentrated sulphuric acid and caustic alkalis.

The *methyl ether*, prepared by the potassium carbonate-methyl iodide method, was crystallised from rectified spirit in colourless rectangular prisms, m.p. 79-81°. (Found: C, 72·2; H, 7·1. $C_{14}H_{16}O_3$ requires C, 72·4 ; H, 6·9 per cent).

Attempted Butyrylation of Orcacetophenone Monomethyl Ether.

Orcacetophenone monomethyl ether (2 g.), sodium butyrate (6 g.) and butyric anhydride (20 c.c.) were refluxed for 8 hours at 180-90°. The reaction mixture on working up as before gave thick brown oil which charred on an attempt at distillation. It did not give any crystals on treatment with various solvents.

(2' : 4'-Dimethoxy-6'-methyl)-benzoyl-butyrylmethane.—Orcacetophenone dimethyl ether (6 g.) and ethyl butyrate (13 g., approx. 4 mols) were added to pulverised sodium (1·5 g., approx. 2 mols.) After the initial vigorous reaction had subsided the reaction mixture was heated in an oil-bath at 115-20° for 1½ hours. On working up as before, a brownish oil was obtained which distilled at 220-25°/20-25 mm. to a pale yellow oil (4 g.). It gave deep reddish violet colouration with alcoholic ferric chloride. (Found: C, 68·9; H, 7·9. $C_{15}H_{20}O_4$ requires C, 68·2 ; H, 7·6 per cent).

The *copper salt*, prepared from the above β-diketone and copper acetate, was crystallised from benzene in dark bluish green needles, m.p. 175-77°. [Found : Cu, 11·1. $(C_{15}H_{19}O_4)_2$ Cu requires Cu, 10·8 per cent].

7-Methoxy- 2-propyl- 5-methylchromone.—The above β-diketone (2 g.) was kept for 40 hours with hydrobromic acid solution (d 1·78, 7 c.c.) and

then poured into water. The product obtained was treated with dilute sodium hydroxide solution. This, however, gave nothing on acidification. The alkali-insoluble portion, after thorough washing with water, was crystallised from dilute alcohol in rectangular prisms (0·8 g.), m.p. 9.-98°. (Found : C, 72·4 ; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4 ; H, 6·9 per cent).

7-Hydroxy- 2-propyl- 5-methylchromone (III, R=C_3H_7).—The above methyl ether (0·5 g.) was dissolved in acetic anhydride (3 c.c.) and refluxed with hydriodic acid solution (d 1·7, 3 c c.) for 1 hour in an oil-bath at 145-55°. The product, obtained on pouring the reaction mixture into sodium bisulphite solution, was treated with dilute sodium hydroxide solution. The portion, insoluble in alkali, was found to be the undemethylated methyl ether. The product, obtained on acidification of the alkaline solution with hydrochloric acid, on crystallisation frcm rectified spirit gave needles, m.p. 163-65°. (Found : C, 71·7; H, 6·5 $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4 per cent).

All the analyses recorded are microanalyses. Furthcr work on the Kostanecki-Robinson reaction on various *o*-hydroxy-ketones is in progress.

SULPHONAMIDES. PART I.

By Gurcharan Lal Juneja, Kartar Singh Narang
and Jnanendra Nath Ray.

Some of 5-, 6- and 8- sulphonamidoquinolines have been synthesised. Some of the compounds have been tested on mice infected with pneumococci and encouraging results have been obtained.

M. B. 693 has found an extensive use in medicine and has proved very efficacious in the treatment of certain infectious diseases, particularly in the treatment of pneumonia. This drug contains p-aminobenzene-sulphonylamino group attached to a pyridine ring. It was thought interesting to synthesise compounds the type (I), because such a side-chain is known to lower toxicity.

$$R(CH_2)_n \cdot CO \cdot NH \langle \rangle SO_2 \cdot NH$$

(I)

where $R = NEt_2$ or $-N\langle \rangle H_2$; $n = 1$ or 2.

The group, $R(CH_2)_n CONH-C_6H_4SO_2NH$, has been introduced in 5, 6 or 8 position of the quinoline molecule. (*cf.* Bobranski, *Arch. Pharm.*, 1939, **277**, 75)

For this purpose p acetylaminobenzenesulphonyl chloride has been condensed with aminoquinolines. For example, with 6-aminoquinoline it gives 6-(p-acetylaminobenzenesulphonamido-) quinoline(II, R=COMe), which

$$RNH \langle \rangle SO_2 \cdot NH$$

(II)

has been hydrolysed to the related amine (II, R=H). The chloroacetyl derivative (II, R=CO·CH₂Cl) cf which, when condensed with diethylamine or piperidine, gives the desired compounds of the general formula (I).

Some of these compounds have been tested on mice infected with pneumococci III and have given results which compare very favourably with M.B. 693. These details will be published elsewhere.

Experimental.

6 (p-*Acetylaminobenzenesulphonamido*)-*quinoline*.—A solution of 6-aminoquinoline (0·52 g.) and p-acetylaminobenzenesulphonyl chloride (0·46 g.) in dry chloroform (75 c.c.) was heated on a steam-bath for ½ hour, when a brownish yellow product separated out. Chloroform was decanted off and the residue, after trituration with water, was crystallised from alcohol (animal charcoal) in colourless transparent plates, m.p. 283°, yield 0·5 g. (Bobranski records m. p. 282°). (Found: N, 12·04. C₁₇H₁₅O₃N₃S requires N, 12·3 per cent).

6 p-*Aminobenzenesulphonamidoquinoline* (II, R=H).—A mixture of the foregoing acetylamino compound (0·5 g) and hydrochloric acid (10 c.c., d 1·15) was refluxed on the steam-bath for 10 minutes. The cooled solution was basified with ammonia when the amine was obtained as a pale yellow product. This was crystallised from dilute alcohol in colourless rectangular plates, m.p. 200°, yield theoretical. (Bobranski records m. p. 201°) (Found : N, 13·42. C₁₅H₁₃O₂N₃S requires N, 14·0 per cent).

6-p-*Chloroacetylaminobenzenesulphonamidoquinoline* (II, R=COCH₂Cl). —Chloracetyl chloride (1·2 g.) was gradually added to a solution of the amine (3 g.) in dry dioxan (50 c.c.). The mixture was warmed to 70° for 2 minutes and then allowed to cool. The solvent was decanted off and the pale yellow residue washed with a small amount of ice-cold water and then crystallised from glacial acetic acid in colourless small plates, m.p. 166 68° (decomp.). (Found after drying in high vacuum at 120° : N, 10·0. C₁₇H₁₄O₃N₃SCl·HCl requires N, 10 19 per cent).

6 p-*Piperidinoacetylaminobenzenesulphonamidoquinoline*.—A solution of the above substance (4·1 g.) and piperidine (1·7 g.) in absolute alcohol (150 c.c.) was refluxed on the steam-bath for 2½ hours. After removal of the solvent the residue was treated with water when a slight turbidity appeared. Sodium acetate was added to the filtrate and the base extracted with ethyl acetate. The crude base obtained after removal of the solvent solidified on repeated treatment with hot petroleum ether. The substance was finally crystallised from a mixture of benzene and ethyl

acetate (2 : 1) in colourless plates, m.p. 131°. (Found : N, 13·46. $C_{22}H_{24}O_3N_4S$ requires N, 13·21 per cent).

6-(p-*Diethylaminoacetylaminobenzenesulphonamido*)-*quinoline*, prepared in the same manner as the above piperidino compound, crystallised from a mixture of benzene and petroleum ether (1 : 10) in colourless plates, m.p. 137°. (Found : N, 13·13. $C_{21}H_{24}O_3N_4S$ requires N, 13·52 per cent).

6-Substituted derivatives (with $n = 2$) as well as all the 8- and 5- substituted compounds described below were prepared in the same way as the corresponding 6-substituted derivatives ($n = 1$) which have already been described. 6-(p-*Chloropropionylaminobenzenesulphonamido*)- *quinoline hydrochloride* crystallised from acetic acid in light yellow transparent needles. (Found : N, 9·43. $C_{18}H_{16}O_3NSCl·HCl$ requires N, 9·82 per cent .

6-(p-*Piperidinopropionylaminobenzenesulphonamido*)-*quinoline*, obtained in 60% yield, crystallised from benzene, m.p. 198-201°. (Found : N, 12·9. $C_{23}H_{26}O_3N_4S$ requires N, 12·78 per cent).

6-(p-*Diethylaminopropionylaminobenzenesulphonamido*)- *quinoline* was obtained in 80% yield. It crystallised from benzene in colourless plates, m.p. 147 49°. (Found : N, 13·18. $C_{22}H_{26}O_3N_4S$ requires N, 13·15 per cent).

8-(p-*Acetylaminobenzenesulphonamido*)-*quinoline* crystallised from alcohol in transparent rods, m.p. 194°, yield 70%. (Bobranski records m. p. 193°). (Found : N, 12·21. $C_{17}H_{15}O_3N_3S$ requires N, 12·31 per cent).

The amine from the above compound crystallised from dilute alcohol in needles, m.p. 188°, yield quantitative. (Bobranski records m. p. 193·5). (Found : N, 13·56 $C_{15}H_{13}O_2N_3S$ requires N, 14·0 per cent).

8-(p-*Chloroacetylaminobenzenesulphonamido*)-*quinoline hydrochloride*, obtained in 55% yield, crystallised from glacial acetic acid in pale yellow transparent plates, m.p. 220° (decomp). (Found : N, 10·29. $C_{17}H_{14}O_3N_3SCl·HCl$ requires N, 10·19 per cent).

8-(p-*Piperidinoacetylaminobenzenesulphonamido*)- *quinoline*, obtained in theoretical yield, was crystallised from a mixture of benzene and petroleum ether in colourless plates, m.p. 172-73°. (Found : N, 13·53. $C_{22}H_{24}O_3N_4S$ requires N, 13·2 per cent).

8-(p-*Diethylaminoacetylaminobenzenesulphonamido*)- *quinoline*, obtained in 70% yield, crystallised from a mixture of benzene and petroleum ether in colourless plates, m.p. 115-16°. (Found : N, 13·19. $C_{24}H_{24}O_3N_3S$ requires N, 13·59 per cent).

8-(p-*Chloropropionylaminobenzenesulphonamido*)-*quinoline hydrochloride* crystallised from glacial acetic acid in colourless transparent

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prisms, m.p. 228° (decomp.). (Found : N, 10·23. $C_{18}H_{16}O_3N_3SClHCl$ requires N, 9·86 per cent).

8-(p-*Piperidinopropionylaminobenzenesulphonamido*)-*quinoline*, obtained in quantitative yield, crystallised from benzene in colourless plates, m.p. 178°. (Found : N, 12·9. $C_{23}H_{26}O_3N_4S$ requires N, 12·78 per cent).

8-(p-*Diethylaminopropionylaminobenzenesulphonamido*)- *quinoline*, obtained in quantitative yield, crystallised from a mixture of benzene and petroleum ether in colourless rectangular prisms, m.p. 95-96°. (Found : N, 12·7 $C_{22}H_{26}O_3N_4S$ requires N, 13·14 per cent).

5-(p-*Acetylaminobenzenesulphonamido*)-*quinoline*, obtained in 60% yield, crystallised from alcohol (charcoal) in colourless needles, m.p. 254° (decomp.). (Bobranski records m.p. 257·58° decomp). (Found : N, 12·68. $C_{17}H_{15}O_3N_3S$ requires N, 12·32 per cent). The *acetyl* derivative on hydrolysis gave the amine in a theoretical yield. The *amine* crystallised from dilute alcohol in colourless rods, m.p. 226-28°. (Bobranski records m. p. 230°). (Found : N, 14·16. $C_{15}H_{13}O_2N_3S$ requires N, 14·05 per cent). The hydrochloride of the chloroacetyl derivative of the amine, obtained in theoretical yield, was crystallised from glacial acetic acid in yellow plates, m.p. 226°. (Found after drying in high vacuum at 130° : N, 9·89. $C_{17}H_{14}O_3N_3SCl·HCl$ requires N, 10·19 per cent).

5-(p-*Piperidinoacetylaminobenzenesulphonamido*)-*quinoline* crystallised from benzene in small plates, m.p. 217-18°. (Found : N,13·09. $C_{22}H_{24}O_3N_4S$ requires N, 13·2 per cent).

The compounds were tested for antipneumococcal activity on mice infected with type III pneumococci against M.B. 693 as control and very encouraging results were obtained in some cases, details of which will be published elsewhere with other authors.

ON THE CONSTITUTION OF PEDICININ.

By Prafulla Kumar Bose and Phanibhusan Dutt.

On the basis of available data, the structure of pedicinin (the pigment of *Didymo-carpus pedicellata*), advanced by Sharma and Siddiqui, has been criticised. New facts concerning its nature have been brought to light and its character as a dibasic acid has been definitely established. Pedicinin undergoes reductive acetylation, and furnishes on catalytic hydrogenation an unstable yellow tetrahydro derivative which easily parts with two hydrogen atoms giving a stable red dihydropedicinin. Like the parent compound t forms a disodium salt Evidences, both direct and circumstantial, have been adduced in support of a new formula for pedicinin, which is now regarded by the present authors as a chalkone quinone in preference to its earlier representation as 4:5:7-trihydroxy-6-methoxybenzalcoumaranone.

Siddiqui (*J. Indian Chem. Soc.*, 1937, **14**, 703) isolated four crystalline constituents from the leaves of *Didymocarpus pedicellata* (N. O. Gesneracex). The results of a detailed investigation of these compounds have led Sharma and Siddiqui (*J. Indian Chem. Soc.*, 1939, **16**, 1) to assign the following structures to them.

Pedicellin (I)

Pedicin (II)

*iso*Pedicin (III)

Pedicinin (IV)

The claims for the representation of pedicinin as 4:5:7-trihydroxy-6-methoxybenzalcoumaranone (IV) are based on the following experimenta observations :

(*i*) Benzaldehyde is produced by the action of alkali on pedicinin.

(*ii*) Ferric chloride shows a colour reaction which is indicative of three unsymmetrical phenolic OH groups in pedicinin.

(*iii*) Pedicellin (I), the constitution of which has been definitely established as 2:3:4:5:6-pentamethoxychalkone, yields an orange compound m.p. 110°, by loss of three methyl groups on treatment with nitric acid in

glacial acetic acid solution. This substance, called methylpedicinin and represented by the structure (V), suffers further demethylation on short treatment with dilute alkali giving pedicinin (IV).

$(OH)_2$ $\Big\{$ $\begin{array}{c} CO \\ C{:}CHPh \end{array}$ $(OMe)_2$ $\Big($

Methylpedicinin (V)

$\xrightarrow{\text{Alkali}}$

HO —— CO ; MeO —— $C{:}CHPh$; OH ; OH O

Pedicinin (IV)

$\uparrow - {:}CH_3Br$

Pedicin (II) $\xrightarrow{Br_2}$

MeO ... $CO{\cdot}CHBr{\cdot}CHBr{\cdot}Ph$ ... OMe ... OMe

(VI)

(*iv*) Treatment of pedicin with *two* atoms of bromine also leads to pedicinin, the formation of which is assumed to proceed *via* the inter mediate chalkone dibromide (VI).

(*v*) Oxidation of pedicin (II) by potassium permanganate gives benzaldehyde as also pedicinin (IV).

(*vi*) Demethylation of pedicellin gives despedicellin (VII), which is also obtained from pedicin and pedicinin under identical experimental conditions.

(*vii*) Pedicinin furnishes a monoacetyl derivative and a monoammonium salt.

HO — $CO{\cdot}CH{:}CHPh$; HO OH ; OH ; OH

(VII)

A close examination of the available data on the constitution of pedicinin convinced us that the arguments, put forward by Sharma and Siddiqui (*loc. cit.*) to explain the formation and reactions of pedicinin based on the structure (IV), are neither convincing nor conclusive. For instance, the spontaneous elimination of two bromine atoms of dibromopedicin (VI) as methyl bromide is an example of somewhat unusual occurrence. Moreover,

it is highly improbable that the double bond of pedicin, a chalkone deriva-
tive, would escape attack by permanganate and one of the hydrogen atoms
attached to the unsaturated carbon atom of an ethylenic linkage would be
involved in oxidation resulting in a coumaranone derivative (IV). It is
also remarkable that out of the three phenolic OH groups present in
pedicinin, only one would lend itself to acetylation and salt formation. The
formation of despedicellin (VII) from pedicinin (IV) also appears improbable
though not impossible. We, therefore, thought it desirable to re-investigate
the constitution of pedicinin.

Pedicinin was isolated from *D. pedicellata* and was also prepared from
pedicellin by the method of Sharma and Siddiqui. We substantiate
Siddiqui's account of pedicinin as regards its molecular composition, melting
point and other physical properties. Regarding its behaviour towards
various reagents, we are not in entire agreement with the observations of
Siddiqui *et al.* We have, for instance, observed that pedicinin is soluble
in dilute potassium bicarbonate solution at room temperature. Pedicinin
is, therefore, more acidic than what has been supposed. Siddiqui, moreover,
reported the development of an ' *immediate* deep reddish brown ' colour on
treating pedicinin with ferric chloride in alcohol. Much significance has
been attached to this test as indicative of three unsymmetrical OH groups
in positions 4, 5 and 7 of formula (IV). We have not been able to observe
any appreciable change of colour using dilute solutions of pedicinin (in
alcohol) and the reagent.

The hydroxyl groups, as formulated in the proposed structure for
pedicinin (IV), are in the *ortho-para* positions to one another. Consequently
pedicinin should be expected to show strong reducing properties. Contrary
to this expectation, pedicinin has been found to be stable towards alkaline
o-dinitrobenzene (Bose, *J. Indian Chem. Soc., Sir P. C. Ray Birthday Vo .,*
1933, p. 65), chloropentammine cobaltichloride (Shibata and Hattori,
Acta Phytochim., 1930, **5**, 117) and Fehling's solution, all of which are
known to undergo reduction forming characteristic colouration or preci-
pitates, as the case may be, in presence of polyhydroxybenzenes having
ortho-para OH groups. These observations, taken in conjunction with
the strong acidic character and deep colour of pedicinin, led us to suspect
that pedicinin may after all be a quinone derivative and that there may be
some truth in the statement of Price and Robinson (*Nature*, 1938, **142**, 147).
These authors had ventured the suggestion that the pigments of *Didymo-
carpus pedicellata* might be related to dunnione, the colouring matter of
Streptocarpus Dunnii, Mast., in view of the fact that the genus *Didymo-
carpus* is closely related to *Streptocarpus* and the two series of pigments

occur as deposit on the leaves. The inability of Sharma and Siddiqui to support the idea of the English chemists seems to be justified inasmuch as the basic structure of the *Didymocarpus* pigments was proved to be different from that of dunnione. The possibility that pedicinin might be a quinone derivative was, however, not recognised by Sharma and Siddiqui.

We carried out some preliminary experiments in order to establish or disprove the quinone character of pedicinin and the results are given below :

(*a*) The colour of pedicinin disappears to a great extent on heating with aqueous sodium bisulphite solution but is restored by the addition of excess of alkali.

(*b*) An alcoholic solution of pedicinin turns yellow on warming with stannous chloride—hydrochloric acid.

(*c*) Pedicinin undergoes reductive acetylation with great ease forming a colourless acetyl derivative.

These observations imply that pedicinin is a quinone, and assuming a *para*-quinone structure, the pigment may be represented by the extended formula (VIII) or (IX).

(VIII)   (IX)

To decide between these two alternative expressions, pedicinin has been catalytically reduced. It smoothly absorbs *four* atoms of hydrogen giving rise to a yellow product, which rapidly turns red on exposure to atmosphere in solution. The red crystalline compound, isolated, from the solution , melts at 134° and absorbs now only *two* atoms of hydrogen in presence of palladium-charcoal giving the foregoing yellow leuco-compound, which is unstable and is quickly converted into the original substance, m.p. 134°, by spontaneous aerial oxidation. These observations seem to justify our decision in favour of formula (IX), inasmuch as the alternative structure (VIII) should be normally expected to furnish a dihydro derivative. The yellow product is undoubtedly tetrahydropedicinin having the formula (X) which is compatible with its instability ; and the red dehydrogenated

product is dihydropedicinin, which is apparently the quinone (XI). Pedicinin must consequently have one of the alternative structures (XII) or (XIII).

(X)

$-H_2$(oxdn.) ⇌ $+H_2$(redn.)

(XI)

(XII)

(XIII)

(XIII)   Reductive ⟶ acetylation

(XIV)

Of these, compound (XIII) should be expected to behave like a dibasic acid (compare 2:5-dihydroxy-1:4-quinone and its derivatives) and form a disodium salt. In fact we have been able to prepare a disodium salt of pedicinin as also that of dihydropedicinin, m.p. 134°.

It has further been observed by us that dihydropedicellin, prepared by catalytic hydrogenation of pedicellin (I), gives on oxidation with nitric acid followed by hydrolysis of the product with alkali, the identical dihydropedicinin, m.p. 134°. The action of nitric acid on pedicinin is, therefore, a case not only of demethylation but also of oxidation, the chalkone group remaining intact. Analogous instances are by no means rare in chemical literature. Many alkyl ethers of tri- and tetra-hydroxybenzenes are known to undergo conversion into 1:4-quinones by the action of nitric acid. For example 1:2:4:5-tetramethoxybenzene is oxidised to 2:5-dimethoxyquinone

by nitric acid (Schüler, *Arch. Pharm.*, 1907, **245**, 281), which no careful hydrolysis by means of alkali furnishes 2:5-dihydroxyquinone having pronounced acidic character (Knoevenagel and Bückel, *Ber.*, 1901, **34**, 3993). The mechanism of formation of pedicinin from pedicellin is obviously very similar and may be represented thus :

Pedicellin (I) $\xrightarrow{\text{HNO}_3}$

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{MeO} \quad \text{CO·CH:CHPh} \\
\text{MeO} \quad \text{OH} \\
\parallel \\
\text{O}
\end{array}
$$

Methylpedicinin
(XV)

$\xrightarrow{\text{Alkali}}$ (XIII)

Our results, therefore, go to show that the structure (XIII) may with confidence be advanced for pedicinin in preference to the earlier formula (IV), the inconsistency of which has already been commented upon.

E X P E R I M E N T A L.

Isolation of Pedicinin and Pedicellin.—The method of Sharma and Siddiqui was generally followed. We found it, however, more expedient to separate pedicinin from the crude ether extract by washing it with very dilute alkali. For this purpose the diluted ether extract was taken in a vertical glass tube (75 cm. × 1.5 cm.), the tapered lower end of which had been closed by means of a piece of rubber tube and screw clip. A thin stream of 1% aqueous alkali was allowed to drop into the ethereal solution, when it dissolved the acidic constituents including pedicinin during its passage through the ether layer. The dark red aqueous solution was separated from the neutral ether extract, acidified with hydrochloric acid and kept in a cool place. The precipitate was collected after 24 hours, and freed from adhering oil by washing with petroleum ether. The crude pedicinin was washed with hot ethyl acetate and then repeatedly crystallised from chloroform.

The neutral ethereal extract was freed from the solvent on the water-bath under reduced pressure and kept in a refrigerator for 3 to 4 days when the major part of crude pedicellin crystallised out. This was twice crystallised from methyl alcohol, distilled in high vacuum (b. p. 150-55°/0·05 mm.)

and then crystallised repeatedly from ether. The transparent prisms or plates, thus obtained, melted at 93° * and did not depress the m.p. of a pure specimen of pedicellin, which had the same m.p.

Pedicinin formed carmine red needles, m.p. 203° (Siddiqui records m.p. 203°). (Found : C, 63· 76 ; H, 4·3. $C_{16}H_{12}O_6$ requires C, 64·00 ; H, 4·1 per cent).

Action of Nitric Acid on Pedicellin : Formation of Methylpedicinin (XV) *and Pedicinin.*—Methylpedicinin, m.p. 110°, was obtained as the main product by the method of Sharma and Siddiqui when the reaction with nitric acid was allowed to proceed for 40 to 50 seconds. If, on the other hand, the duration of the reaction was extended to 90 seconds, appreciable quantities of pedicinin were formed. Pedicinin was separated from methylpedicinin by taking advantage of the greater solubility of the latter in ethyl acetate. The identity of pedicinin, m.p. 202·5°, obtained directly from pedicellin, with the natural product was established in the usual manner.

Reductive Acetylation of Pedicinin : Formation of Tetraacetyldihydro-pedicinin (XIV).—Pedicinin (100 mg.), acetic anhydride (1 c.c.) and zinc dust (300 mg.) were heated on the water-bath for 2·5 minutes. The colour of the solution quickly deepened to reddish violet and then faded away to pale yellow. The yellow solution was filtered from the zinc dust, which was washed with glacial acetic acid. The combined filtrates were concentrated under reduced pressure to a small volume and then poured into crushed ice. The yellow precipitate was collected and twice recrystallised from dilute methyl alcohol containing a little acetic acid when a colourless semi-crystalline product, m.p. 207-8°, was obtained. Attempts to obtain the compound in well-defined crystalline condition were fruitless. (Found : OMe, 6·62. $C_{24}H_{22}O_{10}$ requires OMe, 6·60 per cent). The acetyl compound is freely soluble in most organic solvents except petroleum ether.

Disodium Salt of Pedicinin.—Pedicinin (140 mg.) was dissolved in a small quantity of aqueous alcoholic sodium hydroxide by warming. To the dark red solution about 4 c.c. of 10% alcoholic sodium hydroxide (free from carbonate) were added. The solution was then diluted with absolute alcohol till a slight turbidity appeared and allowed to stand at room temperature. A gelatinous precipitate soon appeared which changed into a brick-red granular mass on keeping overnight. This was collected and washed with absolute alcohol and ether ; yield 130 mg. (Found: Na, 12·88. $C_{16}H_{10}O_6Na_2$ requires Na, 13·37 per cent). The salt readily dissolves in cold water

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* The m p.'s recorded in this paper are uncorrected. Siddiqui reports m.p. 98° for pedicellin.

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forming a red solution from which the original substance can be obtained by acidification with mineral acids.

Catalytic Reduction of Pedicinin : Formation of Tetra- and Di-hydropedicinin (X *and* XI).—Pedicinin (321 mg.), dissolved in alcohol (50 c.c.), was reduced by means of hydrogen in presence of palladium-charcoal (0·2 g. of 8%), which had been previously saturated with hydrogen. The absorption of hydrogen was very rapid. After 52 c.c. (calc. 53 c.c.) at 30° and 760 mm. had been taken up in course of 20 minutes, absorption practically stopped. The yellow solution was freed from the catalyst. During filtration the colour of the solution rapidly changed to deep red apparently due to aerial oxidation. The solution was concentrated under reduced pressure and cooled when dark rectangular plates were obtained. Purified by recrystallisation from dilute methyl alcohol it had m.p. 134° not raised by further crystallisations. (Found C, 63·26 ; H, 5·0 ; OMe, 10·32. $C_{16}H_{14}O_6$ requires C, 63·57 ; H, 4·63 ; OMe, 10·26 per cent). Yield almost quantitative.

Catalytic Reduction of Dihydropedicinin.—An alcoholic solution of the above compound (170 mg.) absorbed 14 c.c. of hydrogen (calc. 13·8 c.c., 2 atoms of H per molecule) at 27° and 760 mm. in presence of palladium-charcoal (0·1 g. of 8%). The red solution turned yellow after reduction and again became deep red on exposure to air as in the foregoing case. From the red solution dihydropedicinin (m.p. and undepressed mixed m.p. 134°) was isolated.

Dihydropedicellin.—Pedicellin (696 mg.) was hydrogenated using palladium-charcoal (0·2 g. of 8%) in alcohol medium. Nearly the theoretical quantity of hydrogen was taken up in course of 25 minutes. The oily residue, left after the removal of the catalyst and the solvent, was distilled at 135-45°/0·1 mm., when a colourless viscous oil was obtained. It could not be crystallised. Yield almost-quantitative.

Oxidation of Dihydropedicellin to Dihydropedicinin (XI).—Dihydropedicellin (638 mg.). dissolved in glacial acetic acid (2 c.c.), was treated with nitric acid (d 1·4, 0·3 c.c.) drop by drop. The red coloured solution was shaken thoroughly and the reaction was allowed to proceed for 90 seconds Ice-cold water was then poured into the reaction mixture and it was extracted with ether. The ether extract was washed with water till free from acid, dried over sodium sulphate and the ether removed. The orange-red, semi-solid residue was warmed with dilute alkali (15 c c. of 5%) on the water-bath till a clear solution was obtained. The red alkaline solution was immediately cooled and acidified with hydrochloric acid. The red precipitate was collected, washed with water, dried and twice crystallised from dilute

methyl alcohol as dark red shining plates, It melted at 134° and was found to be identical with dihydropedicinin, previously described, by direct comparison and by mixed m.p. method ; yield 60% calculated on the amount of pedicellin taken.

The *disodium* salt of dihydropedicinin was prepared by the method already described under the corresponding salt of pedicinin. In this case, however, no gel formation was noticed Yield 300 mg. from 344 mg. of dihydropedicinin. The sodium salt formed orange-red feathery, glistening crystals - having no m.p. below 300°. (Found: Na, 12·67. $C_{16}H_{12}O_6Na_2$ requires Na, 13·3 per cent).

All the specimens were dried at 100-10° in vacuum over P_2O_5 before analyses, most of which were carried out by Mr. N. Ghosh, M.Sc. We offer our sincere thanks to Mr. Ghosh, as also to Dr. S. Siddiqui for the kind gift of a pure specimen of pedicellin.

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VISCOSITY OF THORIUM ARSENATE GELS DURING SETTING

By Mata Prasad and B. G Shejwalkar.

The viscosities of thorium arsenate gel-forming mixtures have been measured during setting, using different amounts of the constituents of the gel-forming mixtures, and adding of extra amounts of electrolytes and non-electrolytes at different temperatures The viscosity-time curves are either rapidly rising ones or are S-shaped. The viscosity at a certain time decreases with (i) an increase of thorium ions in the gel-forming mixture, (ii) the addition of non-electrolytes, and (iii) the increase of temperature But it increases with increase in the amount of arsenic acid and with the addition of extra amounts of electrolytes.

Viscosity changes in a number of gels during the process of setting have been studied in this laboratory (Prasad and Modak, *Proc. Indian Acad. Sci.*, 1940, **11A**, 282). In the present investigation the viscosity of thorium arsenate gels has been measured at different temperatures using different amounts of the constituents of the gel-forming mixtures in presence and absence of extra amounts of electrolytes and non-electrolytes.

Gels of thorium arsenate were prepared for the first time by Prakash and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 587) in an opaque or translucent state from solutions of potassium arsenate and thorium nitrate. Prasad and Desai (*J. Univ. Bombay*, 1938, **7**, III, 132) found that transparent gels of thorium arsenate are obtained if a solution of arsenic acid is used instead of that of potassium arsenate.

EXPERIMENTAL.

The apparatus (constant = 0·0021) used was the same as employed by Prasad and Modak (*loc. cit.*) and the experimental procedure was also the same.

Solutions Used.—Thorium nitrate (6 g.) was dissolved in redistilled water and the solution made upto 100 c.c., thoria content of which was found to be 2·82%.

Merck's extra pure pyro-arsenic acid (10 g.) was dissolved in 100 c.c. of the solution, As_2O_3 content of which was found to be 7. 44%.

Different volumes of the solutions of the two substances along with the addition agents were made to 5 c.c. each, so that after mixing, the total volume of the mixture was always 10 c.c.

R E.S U L T S.

The results obtained are shown graphically in the following figures in which the viscosity of the gel-forming mixtures, expressed in poise (absolute units) are plotted against different intervals of time, expressed in minutes, at which after the gel-formation has commenced, the viscosity readings were taken.

Fig. 1 gives the effect of the addition of different amounts of thorium nitrate (Q) to 0·051 c.c. of the arsenic acid solution at 35°.

Fig. 2 gives the effect of the addition of different amounts of arsenic acid (X) to 5·o c.c. of thorium nitrate solution at 35°.

Fig. 3 gives the effect of temperature on the mixture containing 5·c c.c. of thorium nitrate solution and 0·55 c.c. of the arsenic acid solution.

FIG. I.

Effect of thorium ions.
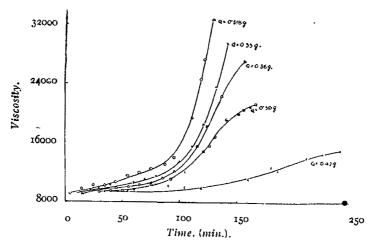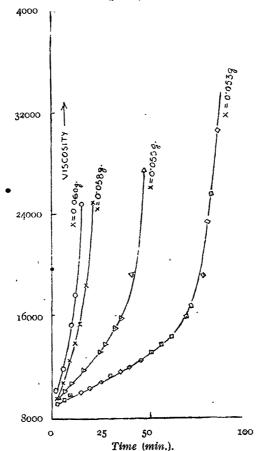
Fig. 4 gives the viscosity-time curves at 35° of gels prepared from different volumes of potassium arsenate solution (12 g. per 100 c.c.) and 9 c.c. of the thorium nitrate solution. On mixing the above-named constituents a precipitate was first formed and it slowly disappeared. The gels formed were turbid. The precipitate reappeared after some time when the readings had to be stopped.

D I S C U S S I O N.
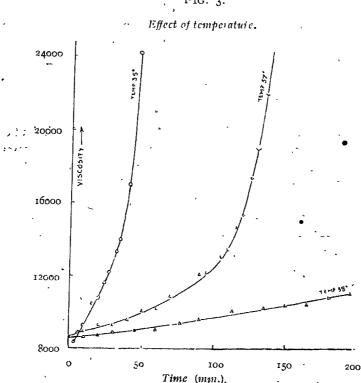
It appears that the general nature of most of the curves shown in Figures 1–4 is essentially the same. All of them at first rise slowly, then

rapidly and in the end most of them tend to run parallel to the axis of viscosity and the others tend to become S-shaped. The absence of any discontinuity in the curves indicates that the various stages involved in the process of the formation of gels do not show their distinct existence. Evidently these stages run simultaneously and lend an aspect of continuity to the whole process of gelation. These conclusions are in conformity with those made by previous workers (Prasad, Modak, Mehta and Desai, *J. Phys. Chem.*, 1932, **36**, 1384, 1938; Mehta, Parmar and Prasad, *loc. cit.*). On plotting log $(\eta - \eta_0)$ against log t, where η is the viscosity at time t and η_0, the viscosity extrapolated from the curves for t equal to zero, the curves obtained are not straight lines, but when values of log $(\eta - \eta_0)$ are plotted against t straight lines are obtained. This shows that the viscosity of thorium arsenate gel-forming mixtures changes with time in the same manner as found by Mardles (*Trans. Faraday Soc.*, 1923, **18**, 327) in the case of gels of methylcellulose in benzyl alcohol.

FIG. 2.

Effect of arsenic acid.

Time (min.).

The rate of change of viscosity with time is greatly altered by a change in the amount of the constituents of the gel-forming mixtures With an increase in the amount of thorium nitrate in the gel-forming mixture, the rate of increase of viscosity decreases considerably (*cf.* Fig. 1). The curves for 0·318 g. and 0·33 g. are rapidly rising ones and they become definitely S-shaped when the amount of thorium nitrate is increased to 0·36 g., 0·39 g., and 0·42 g. indicating the autocatalytic process in gelation. The las-curve (0·42 g.) is a flat "S", showing only small increase in viscosity with time. The retardation of the gelation process as indicated by the curves given in Fig. 1 can be attributed to the peptising action of the thorium ions whereby the density of charge on the micelles and their degree of dispersity are increased. Assuming that the viscosity of the gel-forming mixtures is a function of the size of the micelles and their degree of hydration, the decrease in viscosity at any given interval of time with increase of thorium nitrate in the mixtures, shows that a high density of charge is associated with low degree of hydration. Previous workers have also come to the same conclusion regarding the effect of the metal ions.

FIG. 3.

Effect of temperatuie.

Time *(mm.).*
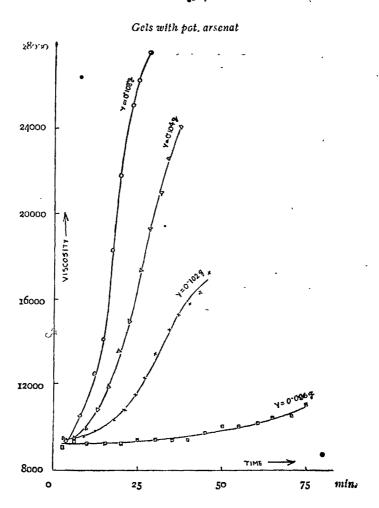
Effect of the addition of increasing amounts of arsenic acid (Fig. 2) is to accelerate the rate of increase of viscosity of the gel-forming mixtures with time. Since increasing amounts of arsenic acid are added to the same amount of thorium nitrate, it is reasonable to expect that the amount of thorium arsenate formed in the gel-forming mixture is increased thereby. Such an increase may cause an increase either in the number of the micelles or their size or both. It also effects a decrease in the concentration of the peptising ions which, in turn, causes a decrease in the density of charge and an increase in the degree of hydration of the micelles. The latter effect suggests that the addition of increasing amounts of arsenic acid causes preferably an increase in the size of the micelles.

Addition of extra amounts of solutions of KCl and $BaCl_2$ increases the rate of increase of viscosity with time (curves not shown). These results are expected normally because such an addition would accelerate the rate of coagulation of the micelles or probably the micelles formed in the presence of extra amounts of electrolytes would not have a large density of charge. A comparison of the effect produced by adding the same volume of solutions of KCl and $BaCl_2$ of the same normality gives the expected result that $BaCl_2$ effects greater increase in viscosity than KCl.

Addition of alcohols and glycerine decreases the rate of increase of viscosity with time and this effect is enhanced as the amount of non-electrolyte added to the mixture is increased. It is very marked in the case of glycerine which practically completely retards large changes in viscosity. This behaviour of non-electrolytes is similar to that observed by previous workers. The observed retarding effect may be due to an increase in the density of charge on the micelles either on account of the diminution of the dielectric constant of the medium or on account of the preferential adsorption of the peptising agent by the micelles in presence of the non-electrolytes. However, it is also possible that the rate of coagulation of the sol of the gel-forming substance is decreased on account of an increase in viscosity on the addition of non-electrolytes. The last mentioned effect seems to be important as it has been observed that the various curves (not shown) are coincident in the early stages.

The rise in temperature causes a decrease in the rate of increase of viscosity during gel-formation. This effect is considerable as evident from Fig. 3 which shows that the rapidly rising curve at 35° becomes almost flat by a rise in temperature by 3°. Prasad and Desai (*J. Indian Chem. Soc.*, 1939, **16**, 3) and Prakash (*ibid.*, 1932, **9**,193) also observed a decrease in the time of setting of thorium arsenate gels with rise in temperature. This effect of temperature is peculiar to the gels of thorium arsenate as in

FIG. 4.

Gels with pot. arsenat

all other inorganic gels it has been found that the time of setting increases on increasing the temperature. Attempts are being made to find an explanation for this peculiarity.

The gels prepared from thorium nitrate and potassium arsenate are very different in character from those obtained by the use of arsenic acid. The former are invariably turbid but their turbidity decreases as larger amounts of thorium nitrate are used. This observation again points to the great peptising action of thorium ions. The viscosity-time curves obtained with smaller quantities of potassium arsenate show very small changes in viscosity. When the quantity of potassium arsenate is increased

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these curves first become S-shaped and then rapidly rising ones. These results are in accord with the discussion given above.

CONCLUSION.

The results given above show that the viscosity method can be employed to study the process of gelation and comparable results can be obtained to show the changes which occur in the process when the condition of the formation of gels, such as the concentration of the constituents of gel-forming mixtures, the temperature, the presence of non-electrolytes, electrolytes and others, are altered. The formation of thorium arsenate gels under various circumstances given above is shown by this method to be a continuous process and no indications have been obtained to bear out the suggestion of any separate existence of different stages involved in the process of gelation.

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MAGNETIC EVIDENCE REGARDING THE STATE OF METALLIC IONS IN PHOSPHATE GLASSES.

By S. S. BHATNAGAR, B. D. KHOSLA AND RAM CHAND.

The nature of the polyvalent ions in phosphate glasses, especially Mn, Co and Ni has been investigated. The manganese in the reduced colourless glasses is in a bivalent state of combination The pink-violet colour of manganese glasses is due to trivalent manganese ions. Cobalt ions do not suffer any change on reduction. The blue colour of coblat glasses and the yellow colour of nickel glasses are attributed to bivalent cobalt and nickel respectively and when the latter are reduced, the glass becomes opaque due to the formation of metallic nickel

There has been much speculation as regards the agents responsible for the colours of various precious stones and minerals. Manganese has long been supposed to be the source of the colour of the amethyst (Berthelot, *Compt. rend.*, 1906, **143**, 477), although the latest evidence attributes the colour to iron rather than to manganese. According to Sir Herbert Jackson (*Nature*, 1927, **120**, 303) none of these views is conclusive. Mellor ("A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 1935, VI, 523) states that manganese colours alkaline glasses pink to violet under oxidising conditions. According to Thorpe ("Dictionary of Applied Chemistry", 1912, II, 721) the full colour is only developed when manganese is in a fully oxidised condition (Mn^{iv}). In Fuwa's opinion (*J. Japan Ceramic Assoc.*, 1923, **366**, 80) the manganic oxide is responsible for the pink colour and bivalent manganese for the decoloured glass.

Notable contributions on the subject have been made by Bancroft and Nugent (*J. Phys Chem.*, 1929, **33**, 481), Solomin (*Keram. i. Stekio*, 1932, **8**, iii, 28), Childs and co-workers (*J. Soc. Glass Tech.*, 1931, **15**, 172), Turner and Weyl (*ibid.*, 1935, **19**, 208), Hoffmann (*Glass*, 1926, **13**, 419, 423, 433) and others. Bancroft, while studying manganese-borax beads from the point of view of their oxygen availability, has concluded that the pink-violet colour is due to trivalent manganese present probably in the form of free manganic oxide, and that the manganese in the colourless reduced glass is bivalent and is in combination as manganous borate. An attempt has been made by us to clarify the issues by the aid of magnetic susceptibility measurements, since the magnetic susceptibilities of ions of an

element in different states of valency can be calculated on the well known Stoner and Van Vleck formula,

$$\chi_{\mathrm{M}} = \frac{N\beta^2}{3kT}[4S(S+1) + L(L+1)]$$

where values of S and L are determined by the valency state of the element. A preliminary note on the subject has been published by one of us (Bhatnagar, *Nature*, 1939, **143**, 599) and it has been shown that manganese in the decolorised borax and phosphate glasses is bivalent and that in the coloured one is a mixture of bi- and trivalent states. The nature of the colorant ions in phosphate glasses, especially manganese, which could not be established, has been thoroughly investigated and a study of nickel and cobalt glasses has also been included in the present investigation.

EXPERIMENTAL.

The melts were made from pure crystallised microcosmic salt in an electric furnace which could be made muffle or open to the atmosphere at will. MnO_2 made by heating analytically pure $Mn(NO_3)_2$ was used. The melts were reduced with ashless tartaric acid to colourless state in the closed muffle. Other ions in turn were also introduced in the blank glass as pure oxides. Platinum dishes were used to avoid entry of all possible impurities. The colour conditions of the melts could be determined at any moment by taking out a bead on a platinum wire. The melts prepared were cooled in a desiccator and finely powdered in an agate pestle and mortar before the susceptibility measurements were made on a magnetic balance of the Guoy type.

Analysis of Glasses.

Manganese.—In order to determine accurately the amount of manganese in the various melts, a slight modification had to be made in the bismuthate method reported by Park (*Ind. Eng. Chem.*, 1926, **18**, 597). It was found that the presence of phosphates from the glasses hindered the estimation of manganese and therefore the phosphates were removed by treating the aqueous solution of the glass with $12\frac{1}{2}\%$ NaOH and 30% H_2O_2 followed by boiling when manganese was precipitated as an impure hydrated oxide free of the phosphate and could be filtered off on a sintered glass filter.

The precipitate thus obtained was dissolved in acidified $FeSO_4$, excess of which was converted to ferric sulphate with H_2O_2 whose excess, in turn was destroyed by boiling. Solution thus prepared was treated with sodium bismuthate and the manganese estimated from the resulting permanganate.

Cobalt.—The presence of phosphates was found to interfere in the estimation of cobalt as well by the α-nitroso-β-naphthol method and they had to be removed by first oxidising cobalt to cobaltic oxide with 30% H_2O_2 in presence of $12\frac{1}{2}$% NaOH. This could then be dissolved in hydrochloric acid and estimated.

Nickel.—Nickel was estimated by the dimethylglyoxime method which worked successfully even in the presence of the phosphates.

Several melts of the blank glass were prepared under different conditions of length and nature of heating and cooling and their susceptibilities were checked against those of KCl and NaCl, values of which are definitely known. The susceptibility values of the various blank glass melts were all within experimental error (-0.389 to -0.391×10^{-6}). The average value -0.390×10^{-6} was taken for calculating the ionic susceptibilities given in the following tables.

TABLE I.

Reduced colourless manganese glasses. (30°)

No.	Mn.	χGlass.	χMn (ionic).
1.	1.265%	2.916×10^{-6}	261.0×10^{-6}
2.	2.150	5.213	260.2
	2.413	2.925	261.0 Mean 260.7

TABLE II.

Coloured manganese glasses. (25°).

No.	Mn.	χGlass.	χMn (ionic).	No.	Mn.	χGlass.	χMn (ionic).
1.	1.40%	3.144×10^{-6}	252.10×10^{-6}	4.	2.36%	5.593×10^{-6}	253.1×10^{-6}
2.	1.99	4.580	249.3	5.	2.61	6.236	253.5
3.	2.10	4.870	250.0	6.	3.63	8.824	253.4
				7.	3.90	9.390	250.3

TABLE III.

Cobalt glasses (without reduction, 30°).

No.	Co.	χglass.	χ co(ionic).	No.	Co.	χglass.	χ co(ionic).
I.	1·231%	1·710 × 10⁻⁶	170·2 × 10⁻⁶	3.	2·33	3·572 × 10⁻⁶	169 6 × 10⁻⁶
2	2 271	3·474	169·7	4.	3·30	5·225	169·7

TABLE IV.

Cobalt glasses (reduced, 20°).   Nickel glasses (without reduction, 20°).

No.	Co.	χglass.	χ co(ionic).	No.	Ni.	χglass.	χ co(ionic).
I.	1·325%	1·866 × 10⁻⁶	169·9 × 10⁻⁶	I.	1 148%	0·536 × 10⁻⁶	80 20 × 10⁶
2	2·010	3·034	170·1	2.	2·689	1·778	80·21
3.	2·428	3·739	169·5	3.	3·316	2·276	80 00

TABLE V.

Calc. values of ionic susceptibilities on Stoner-van Vleck formula × 10⁶

Temp.	Mn⁻⁺	Mn⁺⁺⁺ L-not operative.	Mn⁺⁺⁺ L-operative.	L-operative.	Co⁺⁺ L-not operative.	L-not operative.	Ni.⁺⁺ L-operative
30°	260·6						
25°	265·3	181·9	227·3				
20°				107·7	193·8	57·72	144·3

DISCUSSION.

Manganese Glasses.

Calculating the ionic susceptibilities of manganese from the Stoner-Van Vleck formula for bivalent manganese, which is in the ^6S state, the orbital moment L equals zero, the spin moment S has a value 5/2, and the ionic susceptibility at 30° works out at $260·6 \times 10^{-6}$. This value is in close agreement with mean value of $260·7 \times 10^{-6}$ obtained experimentally in Table I The decolorised glass when viewed in the ultraviolet light from a mercury vapour lamp with a Wood's filter, showed an orange-red fluorescence, identical with that of the anhydrous manganous halides. These observations prove that manganese in the colourless glass is in bivalent state of combination.

As regards the coloured manganese glasses it has been believed by most workers that it is the trivalent manganese which is responsible for the pink-violet colour. The trivalent manganese is in $^5D_0$ state. Spin moment L also is 2. It has been noted by Sommerfeld ("Atombau", 4th Ed p. 639), Bose (Z. Physik, 1927, 43, 864), Stoner (Phil. Mag., 1929, 8, 250) and others that for ions of the iron group, the L-moment is fully quenched and its value is zero. Calculating on this basis we find that the ionic susceptibility for trivalent manganese works out to 181.9×10^{-6} at 25°. If the orbital moment were not quenched, the other limiting value for fully operative L-orbital moment is 227.3×10^{-6}. As shown in Table II the experimental values range between those of the bivalent $(265.3 \times 10^{-6}$ at 25°) and trivalent states. This gives one good reason to believe that it is a mixture of the bi- and trivalent manganese compounds which is responsible for the various shades of colour.

To find out how much exactly of each state is present, available oxygen in the first five samples of Table II was found out. For this purpose a a certain weight of the glass (2.5 to 3.0 g.) was covered in an Erlenmeyer flask with a known excess of standard ferrous ammonium sulphate solution, and left to dissolve gradually. When the glass completely disappeared the quantity of the reducing agent consumed was found out and the available oxygen calculated from it. To avoid errors of oxidation by the atmosphere a blank was always titrated alongside and use of heat for quickening the solution of glass was avoided.

TABLE VI.

No.	Manganic ions in total Mn.	χ_{ionic} (calc.)		χ_{ionic} (obs).
		L-operative.	L-quenched.	
1.	14.5%	259.5×10^{-6}	253.2	252.1×10^{-6}
2.	15.2	259.2	252.5	249.3
3.	13.1	259.9	254.2	250.0
4.	12.6	260.2	254.5	253.1
5.	12.7	260.1	254.4	253.5

As is clear from Table VI, the observed values of susceptibility of the manganese ions are in fairly good agreement with the calculated ones for a mixture of manganous and manganic ions, L-orbital moment being fully quenched for the manganic ions. Since we have found that the bivalent manganese gives colourless glass, it must be the trivalent ions which are responsible for the pink-violet colour,

Cobalt Glasses.

It is a well known fact that when cobalt-borax or microcosmic beads are exposed to the reducing flame there is no change in colour. The susceptibility values given in Tables III and IV for the glass, made in free excess of air and one reduced with tartaric acid, are practically identical. This confirms that there is no change in the nature of cobalt ions. Furthermore these susceptibilities are intermediate between the two limiting values calculated for the bivalent cobalt ions shown in Table VI, which must be responsible for the blue colour of the cobalt glasses.

Nickel Glasses.

Nickel was found to colour the phosphate glasses yellow. The ionic susceptibilities found for nickel ions as given in Table IV are between the limits calculated for the bivalent nickel with L-moment operative and quenched. This indicates that the yellow colour is due to the bivalent nickel ions. When nickel glasses were reduced with tartaric acid, they yielded an opaque mass which was ferro-magnetic in nature and indicated presence of metallic nickel.*

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* These values observed by us for bivalent cobalt and nickel ions in the phosphate glasses are in line with those obtained by Bhatnagar, Khana and Nevgi (*Phil. Mag*, 1938, 8, 250) for certain other salts of cobalt and nickel.

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NITROGEN FIXATION AND TOTAL BACTERIAL COUNT ON THE APPLICATION OF ENERGY MATERIALS TO ALKALI SOILS.

By N. R. Dhar and E. V. Seshacharyulu.

Nitrogen fixation in alkali soils on the addition of energy materials like carbo-hydrates has been studied   As in the case of normal soils, nitrogen fixation takes place in the alkali soils and it is always greater in the soils exposed to sunlight than in those kept covered although the total bacterial numbers are smaller in the former than in the latter. The nitrogen fixed per g. of carbon oxidised is greater in the soils exposed to light than in the covered ones and the order of fixation is more or less the same as that obtained with normal soils.

There are vast tracts of alkali soils in different parts of India.   It is estimated that the total area of alkali land (*Usar*) in the United Province alone is over five millions of acres.   The chief defects of such a soil have already been reported in an earlier communication (Dhar, *J. Indian Chem. Soc. Ind. & News Ed.*, 1939, **2**, 105).   The following results show the difference between a normal soil and an alkali soil.

TABLE I.

	Total nitrogen.	Total carbon.	p_H.	Total bacteria in millions per g. of dry soil.
Alkali soil collected from Bani near Allahabad	0·0336 %	0·2301 %	10·5	0·12
Normal soil Allahabad	0·0516	0·5304	7·8	13·3

The object of this investigation is to ascertain whether nitrogen fixation takes place in the alkali soils, as in the case of normal soils, when treated with carbohydrates. The experiments were carried on with soil collected from Bani (near Allahabad).   The carbohydrates used were chemically pure canesugar, glucose and fructose.

EXPERIMENTAL.

The alkali soil (1 kg.) was mixed thoroughly with each of the above-mentioned energy materials (29 g.) and 250 c.c. of water in enamelled basins (diameter 26 cm.).   The experiments were carried out in duplicate.   Control

experiments were also performed with alkali soils without the addition of carbohydrates. One set of basins was exposed to sunlight daily for eight hours and the other corresponding set, covered loosely with a double layer of thick black cloth to exclude light, was also kept side by side along with the exposed basins to eliminate the temperature effect. Water (160 c.c.) was added twice a day to the exposed soils and once to the soils covered to maintain a uniform moisture content. Before commencement of the experiments estimations of total nitrogen, total carbon and total bacterial numbers of the original soil were made. At regular intervals the total nitrogen, total carbon and total bacterial numbers of the exposed and covered soils were determined simultaneously. The following results are the mean of the duplicate experiments.

TABLE II.

1 Kg. of soil + 20 g. of canesugar.
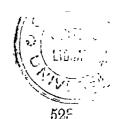
Date.	Total N.	Total C.	Total bacteria.*	Total N.	Total C.	Total bacteria*.
	Exposed			Covered.		
29-12-1937 Original soil	0·0336%	0·2301%	0·12%	0·0336%	0·2301%	0·12
Immediately after mixing	0·0336	1·0612	—	0·3336	1·0596	—
17-1-38	0·036	0·01612	8·2	0 0348	0·9403	10·3
8-2-38	0·038	0·7066	22·4	0·0364	0·7894	39·5
8-3-38	0·039	0·5318	10·7	0·0364	0·6427	28·4
4-4-38	0·0396	0·432	9·1	0·0364	0 5135	23·6

TABLE III.

1 Kg. of soil + 20 g. of glucose.

Date.	Total N.	Total C.	Total bacteria.*	Total N.	Total C	Total bacteria.*
	Exposed.			Covered.		
29-12-37 Original soil	0·0336%	0·2301%	0·12	0·0336%	0·2301%	0·12
Immediately after mixing	0·0036	1·0214	—	0·0336	1·0286	—
21-1-38	0·036	0·8579	6·2	0·0348	0·8926	7·1
10-2-38	0·0376	0·6849	23·6	0·0356	0·7529	36·8
10-3-38	0·039	0·5411	12·0	0·0356	0·6041	27·5
6-4-38	0·0399	0·419	8·9	0·0366	0·4601	28·8

* (millions/g of dry soil).

Similar results were obtained with fructose. In the control soils without the addition of carbohydrates, there was a slight fall of nitrogen, carbon and bacterial numbers.

The following table shows the amount of nitrogen fixed per gram of carbon oxidised both in alkali and normal soils.

TABLE IV.

	Alkali soil		Normal soil	
	Exposed.	Covered.	Exposed.	Covered
Canesugar	9·5	5·1	—	—
Glucose	9·9	5·2	12·5	6·5
Fructose	11·3	5·6	11·9	6·8

A NOTE ON THE REACTIONS AND EXCHANGE OF ACTIVE IODINE IN INORGANIC SYSTEM.

By Shyamadas Chatterjee and Priyadaranjan Râẏ.

Experiments with natural radio-elements have established complete exchange of activity between atoms existing in the same valence type in the compounds and no exchange between atoms in the ionic and co-valent state. But with artificially produced active elements quite different results have been reported. Exchange of active iodine between sodium iodide and methyl iodide or iodoform in alcohol or acetone has been observed by McKay (*Nature*, 1937, **139**, 283), it being immaterial which component of the system was active originally. Similar results have been obtained by other workers as well (Juliusburger, Topley and Weiss, *J. Chem. Phys.*, 1935, **3**, 437 ; Hull, Shiflett and Lind, *J. Amer. Chem. Soc.*, 1936,**58**, 535, 1822). In the pure inorganic system it has, however, been found in the case of co-ordination compounds that no exchange occurs between the co-ordinatively bound chlorine within the complex zone and the ionic chlorine outside (Ettle and Johnson, *J. Chem. Soc.* 1939, 1490). It was, therefore, considered interesting to examine such exchange reactions between co-valently and co-ordinatively bound atoms within one and the same complex zone, in other words, to explore any possible difference between the primary and auxiliary valencies of a central atom. Artificially produced radio-elements can alone serve as indicators for this purpose.

With radioactive iodine as an indicator we have examined qualitatively the exchange reactions between mercuric iodide and ammonium iodide ; the iodine of the latter compound was rendered active by previous irradiation of its solution with slow neutrons. The resulting complex $(NH_4)_2$-HgI_4 was subsequently decomposed into its components by dilution with a large quantity of water. The precipitated mercuric iodide was found to be active when examined in a Geiger-Muller counter. Similar results were obtained with bismuth and lead iodide which form complex $(NH_4) BiI_4$ and $(NH_4)_2PbI_4$ respectively.

$$x NH_4 I^* + MeI_{4-x} \longrightarrow (NH_4)_x MeI_4^* \longrightarrow x NH_4 I^* + MeI^*_{4-x}.$$

where $Me = Hg$, Bi, or Pb ; I^* represents active iodine atom.

Similar results have also been reported by Polesitzki (*Compt. rend.*

Acad. Sci. U.R.S.S., 1939 **34**, 540), in the case of KI and HgI$_2$; the complex K$_2$HgI$_4$ was decomposed by silver nitrate into AgI and HgI$_2$.

The results show that there is no essential difference between the normal co-valency and the co-ordinate co-valency.

Our best thanks are due to Prof. D. M. Bose, Director of the Bose Institute for his kind interest and for the facilities of neutron irradition and radioactive measurements in his Institute.

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A NOTE ON THE OCCURRENCE OF FREE FATTY ACIDS IN THE CAKE OF *PONGAMIA GLABRA.*

By N. V. Subba Rao and J. Veerabhadra Rao.

The seed-cake of *Pongamia glabra* has been recommended by Desai Sudborough and Watson (*J. Indian Inst. Sci.,* 1923, 6, 93) as a good manure owing to its high nitrogen content. Later Srinivasan and Subrahmanyan (*ibid.,* 1934, 17, 49) isolated a protein from the seed-cake using sodium carbonate solution as solvent. They have found use for this protein in the preparation of water paints. Apart from this, no systematic study of the seed-cake seems to have been made.

The seed-cake, obtained by pressing out the oil from the seeds in a country press, was extracted with petroleum ether and the extract on concentration yielded a colourless waxy substance (0·7%). On close examination it was found to be a mixture and one of the components could be easily separated on account of its sparing solubility in hot petroleum ether. This product could be identified as karanjin from its well known properties. The petroleum ether-soluble fraction yielded a waxy substance, which melted at 73·5-75°. The acid number and saponification value (162·0 and 162·4 respectively) of the substance agreed very closely, thereby showing that it consists mostly of fatty acids. The iodine number of the product was very low indicating that the acids were highly saturated. On saponification and extraction of the dry soap with petrol very little non-saponifiable matter was obtained and the mixed fatty acids liberated from the soap exhibited the same properties as the original substance. It is interesting to note that the seed-cake of *Pongamia glabra* yields almost completely saturated fatty acids having a mean molecular weight of 345·5.

The fatty acids obtained have been small in amount and, therefore, a regular separation of the components by the fractionation method could not be effected. The melting point, saponification equivalent and iodine number indicate the acids to belong to saturated higher fatty acids above stearic in the series. The mixture of fatty acids is readily soluble in ether at the laboratory temperature and at 16° 0·5 g. of it dissolves in 30 c.c. of ether (behenic acid has very low solubility—0·19 g. in 100 c.c. of ether at 16°, whereas arachidic and lignoceric acids are readily soluble

in ether). Attempts made to effect the separation of the acids either by fractional crystallisation or through their salts were not successful. From the available data, the mixture appears to consist primarily of arachidic and lignoceric acids. In view of the fact that arachidic, behenic and lignoceric acids have been reported to be present in the oil (Manjunath and Rao, *J. Indian Chem. Soc.*, 1938,, **15**, 653) the mixture may contain behenic acid also but this must be only in a very small amount.

The isolation of these fatty acids from the seed-cake offers an explanation of the results obtained by previous workers on the expelled oil (Desai *et al, loc. cit.*) and solvent-extracted oil (Grimme, *Chem. Rev.*, 1910, **17**, 233). The results are tabulated below.

Properties of mixed fatty acids

	Acid value.	Sap. value.	I. V.	Titre test.	M.p.	Neut. value	I. V.	Mean M.W.
Expelled oil	6·4	185 7	88 9	29·5		191·8	91·2	292 5
Ether-extracted oil	42 3	185·1	77 3	42·5	43·8	180·1	78·8	308 7

The ether-extracted oil obviously brings along with it these saturated higher fatty acids (free) due to which it has a higher acid value and lower iodine value. The mixed fatty acids liberated from it have a higher melting point and higher mean molecular weight than those obtained from the expelled oil. Further, this oil has been observed on keeping for a week or two to deposit these solid fatty acids admixed with a little karanjin (Rao and Seshadri, *Current Sci.*, 1940, **4** 76), whereas the expelled oil did not do so during the same time.

The results described above definitely indicate the occurrence of saturathe higher fatty acids (free) in the seed, their retention largely by the cake when the oil is pressed out and their presence in the oil when it is obtained by solvent extraction.

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MECHANISM OF THE POLYMERISATION OF THIOCYANOGEN FROM MAGNETIC STANDPOINT.

By S S. BHATNAGAR, P. L. KAPUR AND B D. KHOSLA.

Mechanism of the polymerisation of thiocyanogen to para form has been investigated by studying the paramagnetic property in different solvents *e g.* carbon disulphide, bromoform and *cyclo*hexane of different concentrations.

Thiocyanogen was obtained in the free state by Soderback (*Annalen*, 1919, **419**, 217) by the interaction of iodine with an ethereal suspension of silver thiocyanate. Lecher and Goebel (*Ber.*, 1921, **54**, 2223) determined by cryoscopic method the molecular weight of thiocyanogen in bromoform. Solutions less than half normal indicated thiocyanogen to be dissolved as $(SCN)_2$ but those with higher concentrations gave evidence of polymerisation. When a solution of thiocyanogen in solvents such as carbon disulphide, *cyclo*hexane, bromoform etc. is left for sometime, a brick-red or an orange amorphous mass separates, which is the polymeric form of thiocyanogen known as 'para thiocyanogen'.

The polymerisation of thiocyanogen to the para form can proceed through various stages represented either by (SCN), $(SCN)_2$, $(SCN)_3$, $(SCN)_4$, $(SCN)_5$, $(SCN)_6$......$(SCN)_n$ or by $(SCN)_2$, $(SCN)_4$, $(SCN)_6$, $(SCN)_8$ ......$(SCN)_n$ where n is an even integer *i.e.* through the stages containing molecules having both even and odd numbers of electrons or those having only even number of electrons. The life period of different stages during the course of polymerisation is very short, therefore, methods such as depression in freezing point, elevation of boiling point, etc., cannot be employed with success to explain the mechanism of polymerisation.

Molecules containing odd number of electrons exhibit paramagnetism, whereas those with even number of electrons exhibit diamagnetism. Now, if the polymerisation of thiocyanogen proceeds through the formation of odd molecules, the solution of thiocyanogen at times would exhibit paramagnetism. Therefore the authors in the present investigation have undertaken to investigate the mechanism of polymerisation of thiocyanogen to para form by studying the magnetic property of thiocyanogen in different solvents.

EXPERIMENTAL.

Thiocyanogen in carbon disulphide, bromoform and *cyclo*hexane was prepared by the interaction of silver sulphocyanide and bromine dissolved in these solvents. Pure solvents available from the stores were further purified by the usual methods. Pure bromine was prepared by Scott's method (*J Chem. Soc.*, 1913, **103**, 848), traces of moisture present in it were removed by redistilling it over fused calcium bromide. In each solvent solutions of various concentrations were prepared. The maximum concentrations studied are indicated in Table I. When higher concentrations were prepared, thiocyanogen staited polymerising into the insoluble form immediately. Deposition of the para form was quickest in bromoform and less so in carbon disulphide and *cyclo*hexane respectively.

TABLE I.

Limits of concentration of thiocyanogen for the various solvents.

Carbon disulphide	$0.48 N$
Bromoform	0.33
*cyclo*Hexane	Very low.

Concentration of thiocyanogen was determined by allowing a known volume of the solution to react with excess of KI solution and titrating the liberated iodine against standard sodium thiosulphate solution.

The susceptibilities of the solutions were found on Guoy type balance (*Compt. rend.*, 1889, **109**, 935; *cf.* also Bhatnagar, Mathur and Kapur, *Indian J. Phys.*, 1928-3, 153) and were checked on Decker magnetic balance (*cf.* Bhatnagar, Nevgi and Tuli, *Indian J. Phys.*, 1935, **9**, 311). The susceptibility of thiocyanogen in solution was calculated from the relation

$$\chi_{thiocyanogen} = \frac{\chi_{soln.} - (1 - p/100)\chi_{\,solvent}}{p/100}$$

where p represents the weight of thiocyanogen in 100 g. of the solution. If left to evaporate all the solutions eventually deposited the orange, insoluble para thiocyanogen which was diamagnetic. The results of the various measurements are tabulated below.

TABLE II.

Magnetic susceptibility of thiocyanogen from fresh
solutions in carbon disulphide.

Temp. $= 18°$.

No.	Colour.	Density.	Normality.	%SCN.	χ_{soln}.	Susceptibility Specific.	Mol.
	Colourless	1·270	0	0	$-5·500 \times 10^{-7}$	—	—
1.	Light yellow	1·278	0·48	2·19%	$-5·476$	$-4·42 \times 10^{-7}$	$-57·28 \times 10^{-6}$
2.	,,	1·276	0·42	1·92	$-5·480$	$-4·21$	$-48·84$
3.	,,	1·274	0·40	1·82	$-5·459$	$-3·25$	$-38·70$
4.	,,	1·274	0·39	1·77	$-5·461$	$-2·96$	$-34·74$

TABLE III.

Magnetic susceptibility of thiocyanogen from carbon disulphide.

Solutions kept for 24 hours.

Temp. $= 20°$.

No.	Colour.	Density.	Normality.	%SCN.	χ_{scln}	Sp. Susceptibility.
1.	Light yellow	1·273	0·082	0·37%	$-5·251 \times 10^{-7}$	$+6·18 \times 10^{-}$
2.	,,	1·273	0·076	0·35	$-5·341$	$+4·00$
3.	,,	1·272	0·060	0·27	$-5·421$	$+2·51$

TABLE IV.

Magnetic susceptibility of thiocyanogen from solutions in bromoform.

Temp. $= 20°$.

No.	Colour.	Density.	Normality.	%SCN.	χ_{soln}.	Susceptibility Sp.	Mol.
	Colourless	2·888	0	0	$-3·160 \times 10^{7}$	—	—
1.	Yellow	2·815	0·33	0·679%	3·158	$-0·410 \times 10^{-6}$	$-47·56 \times 10^{-6}$
2.	,,	2·820	0·31	0·638	3·165	$-0·410$	$-47·56$
3.	,,	2·832	0·25	0·513	3·166	$-0·410$	$-47·56$

TABLE V.

Magnetic susceptibility of thiocyanogen from solutions in cyclohexane.

Temp. = 20°.

No.	Colour.	Density.	Normality.	%SCN.	$\chi_{soln.}$	$\chi_{thiocyanogen}$
—	Colourless	0·7750	0	0	$8 \cdot 100 \times 10^{-7}$	
1.	Red	0·7751	0·02 to 0·03	0·25	8·052	$+1 \cdot 08 \times 10^{-6}$
2.	,,	0·7750	,,	0·24	8·053	$+1 \cdot 17$
3.	,,	0·7750	,,	0·24	8·033	$+2 \cdot 00$

TABLE VI.

*Magnetic susceptibility and density of the orange para form
as obtained from different solvents.*

Temp. = 20°

Solvent.	Density.	χ.
Carbon disulphide	1·758	$3 \cdot 36 \times 10^{-7}$
cycloHexane	1·755	3·35
Bromoform	1·762	3·36
		Mean $3 \cdot 36 \times 10^{-7}$

DISCUSSION.

From the results tabulated above, the following points are brought out in prominence:

1. In bromoform solutions with concentrations below 0·5N, thiocyanogen exhibits a constant specific magnetic susceptibility of $-0 \cdot 410 \times 10^{-6}$.

2. In fresh carbon disulphide solution (Table II) of concentration 0·48N and 0·42N the specific magnetic susceptibility of thiocyanogen is $-0 \cdot 442 \times 10^{-6}$ and $-0 \cdot 421 \times 10^{-6}$ respectively, and in solutions of lower concentrations the value decreases. Furthermore, when these solutions are kept overnight, there is a decrease in the concentration due to separation of the insoluble para form and the thiocyanogen then exhibits paramagnetism (Ta ᴵ ᴵᴵᴵ).

3. The *cyclo*hexane solutions are dull red in colour and inspite of the great dilution of the solution, thiocyanogen shows definite paramagnetism (Table V).

4. The specific magnetic susceptibility values and the density measurements of para thiocyanogen as obtained from different solvents show them to be similar in nature.

Kauffmann and Kogler (*Ber.*, 1926, **59**, 178) found that thiocyanogen polymerises with the formation of cyanogen thiocyanate and dithiocyanogen monosulphide, and therefore they assumed that this halogenoid is capable of existing in two tautomeric forms to which they assigned the following structural formulae :

$$\begin{array}{c} S\!-\!C \equiv N \\ | \\ S\!-\!C \equiv N \end{array} \quad \rightleftharpoons \quad S\!=\!S\Big\langle \begin{array}{c} C \equiv N \\ C \equiv N \end{array}$$

(I)   (II)

Brindley (*Phil. Mag.*, 1931, **11**, 786), Kido (*Sci. Reports Tohoku Imf. Univ.*, 1932, **21**, 1), Bhatnagar and Lakra (*Indian J. Phys.*, 1933, **6**, 43) and many others have found that Slater's method of calculating charge distribution gives magnetic susceptibilities in better agreement with experiment than those calculated according to Pauling's method.

When the molecular magnetic susceptibility values for formulae (I) and (II) are calculated by taking into account Slater's values for gram ionic susceptibility of sulphur and Pascal's corrected values for carbon and nitrogen and constitutive correction factor due to each $C \equiv N$ group, we get the molecular susceptibility of (I) by the additivity law to be $-45\cdot90 \times 10^{-6}$ and for the molecular susceptibility of (II), $-64\cdot79 \times 10^{-6}$.

Slater's gram-ionic susceptibilities.

S^{-2}	S^{2}	S^{4}
$-34\cdot36 \times 10^{-6}$	$-12\cdot15 \times 10^{-6}$	$-5\cdot73 \times 10^{-6}$

Pascal's corrected values of susceptibilities.

	χ_A
Carbon	$-6\cdot00 \times 10^{-6}$
Nitrogen	$-5\cdot57$
Constitutive correction factor for $C \equiv N$	$0\cdot77$

The molecular weight of thiocyanogen in bromoform was determined by Lecher and Goebel (*loc. cit.*). Cryoscopic measurements for solutions less than half normal indicated thiocyanogen to exist as $(SCN)_2$. As given in Table IV, the specific magnetic susceptibility of thiocyanogen is -0.410×10^{-6}, and assuming it to exist in the form $(SCN)_2$, its molecular susceptibility comes out to be $-0.410 \times 116 \times 10^{-6}$ or -47.56×10^{-6}.

Comparing the value -47.56×10^{-6} obtained above for thiocyanogen with -45.90×10^{-6} and -64.79×10^{-6}, the values for the two tautomeric forms of thiocyanogen calculated on the Slater's basis, it is clear that in bromoform solutions, less than semi-normal, thiocyanogen exists as $(SCN)_2$. Taking Slater's values to be correct, the percentage of the two tautomers in bromoform solutions works out as $(I) = 91.21\%$ and $(II) = 8.79\%$.

Further, because the value of molecular susceptibility lies between those of the two tautomeric forms of $(SCN)_2$, it is evident that in these solutions thiocyanogen does not ionise to give the free radical SCN. These results are in accord with the cryoscopic determinations of Lecher and Goebel (*loc. cit.*).

The values of molecular magnetic susceptibility of thiocyanogen calculated from freshly prepared $0.48N$ and $0.42N$ solutions in carbon disulphide (Table II) come out to be -51.28×10^{-6} and -48.84×10^{-6} respectively. These values are higher than the values obtained from bromoform solution as well as those calculated for the formula $N \equiv C - S - S - C \equiv N$ (Slater), but less than that calculated for the formula (II)

It is clear from these results that in solutions of concentration $0.42N$ and higher, thiocyanogen shows tendency to tautomerise between formula (I) and (II) and there is 71.5 and 84.4% of (I) in solution of 0.48 and 0.42 normality respectively.

However, the values of molecular susceptibility obtained for slightly more dilute solutions (Table II) are even less than the calculated value for formula (I). This decrease in the value shows that in the fresh dilute solutions, thiocyanogen ionises to give the odd molecules SCN, which being paramagnetic reduce the diamagnetism of the dimolecular form appreciably.

The Bohr magneton value for an odd molecule calculated from the formula $2.839 \sqrt{\chi_M (T - \theta)}$ comes out to be 1.73. Taking θ to be zero for approximation and $T = 293°$ A, the χ_M for a free radical from the equation $1.73 = 2.839 \sqrt{\chi_M \times 293}$ comes out to be 1272×10^{-6}.

In case of thiocyanogen the free radical SCN has a molecular weight 58. Specific susceptibility calculated from $\chi_M = 1272 \times 10^{-6}$ for this free radical would be 21.93×10^{-6}. The specific magnetic susceptibility of $(SCN)_2$ as found in bromoform solution is -0.410×10^{-6}. Assuming the solution of

thiocyanogen in carbon disulphide to be a mixture of SCN and $(SCN)_2$ and calculating on this basis the percentage of free radical SCN in carbon disulphide solution of normality 0·40 and 0·39 would be as given in Table VII.

TABLE VII.

Solvent	Normality.	χ.	Free radical.
CS_2	0·40	$-0·325 \times 10^{-6}$	0·38%
CS_2	0·39	$-0·296$	0·51

When the fresh solutions in carbon disulphide were kept overnight an orange polymer separated out as insoluble deposit and the magnetic susceptibility of the filtered solution exhibited paramagnetism (Table III). The paramagnetic specific susceptibility of thiocyanogen varied from 0·618 to $0·251 \times 10^{-6}$ for solutions of concentration 0·082 to 0·060N respectively. These results show that the polymerisation of thiocyanogen to para form takes place through the various stages represented by SCN, $(SCN)_2$, $(SCN_3$ $(SCN)_4$, $(SCN)_5$.........$(SCN)_n$, and not through $(SCN)_2$, $(SCN)_4$, $(SCN)_6$ ....$(SCN)_n$ where n is an even integer. So that when the solution has an excess of the odd molecules, it exhibits greater paramagnetism than when the concentration of the even molecules is greater. The susceptibility values found out are the net results of these opposing factors.

Solutions of thiocyanogen were also prepared in *cyclo*hexane. Although the concentrations of thiocyanogen were low (0·03N) yet one striking feature noticed in their case was that the solutions were dull red in colour and thiocyanogen was definitely paramagnetic in nature. The colour of the solution, coupled with the definite paramagnetic values obtained for thiocyanogen clearly shows that in these solutions of thiocyanogen there is an appreciable amount of the free radical SCN present. The percentage of the free radical SCN as calculated is given in Table VIII.

TABLE VIII.

Solvent.	Thiocyanogen in the solution.	$\chi_{thiocyanogen}$.	Free radical SCN
*cyclo*Hexane	0·25%	$1·08 \times 10^{-6}$	6·67%
,,	0·24	1·17	7·07
,,	0·24	2·00	10·78

When the solutions of thiocyanogen in various solvents were made to stand for more than 48 hours, all of them deposited an orange coloured

para form. The density measurements of the various samples and the magnetic susceptibility values as given in Table VI show that except for slight variation due to experimental error, the samples are the same in nature. As regards the constitution of this para form nothing is known. Its molecular weight had not been determined due to various difficulties such as its total insolubility in various solvents and decomposition on heating.

Farquharson (*Trans. Faraday Soc.*, 1936, **32**, 219) has found that when cyanogen chloride $Cl-C\equiv N$ polymerises to $(CNCl)_3$ with the replacement of triple bonds by double bonds, the molecular susceptibility of cyanogen chloride polymer decreases.

$$
\begin{array}{c}
Cl \\
| \\
C \\
\diagup\!\!\diagup \quad \diagdown \\
N \qquad N \\
| \qquad \| \\
Cl-C \quad C-Cl \\
\diagdown \quad \diagup \\
N
\end{array}
$$

According to Pascal the bond constitutive effects are

$$-C=N- \qquad +8\cdot2$$

$$-C\equiv N \qquad +0\cdot8$$

so that the disappearance of three $(-C\equiv N)$ bonds should raise the diamagnetic value of susceptibility by 2·4 and the appearance of $3(-C=N-)$ bonds should lower it by 24·6, so that there should be a net decrease of 22·2.

During the polymerisation of thiocyanogen the value of specific magnetic susceptibility has fallen from $-0\cdot410\times10^{-6}$ in bromoform solution to $-0\cdot336\times10^{-6}$ for the para form (Table VI). This fall can be due to the replacement of some of the triple bonds by the double bonds as in the case of cyanogen chloride studied by Farquharson. It may be suggested that the para form may have a structure resembling in some way the structure of polymerised cyanogen chloride.

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PHYSICAL CHEMISTRY OF RESIN SOLUTIONS. PART II. NATURE OF RESIN SOLUTIONS IN ORGANIC SOLVENTS.

By Santi Ranjan Palit.

Solutions of natural resins, particularly shellac in organic solvents like alcohol, acetone, etc. have been found to be non-colloidal since they rapidly dialyse out, pass through ultrafilters easily, are devoid of Tyndall effect and have considerable osmotic properties. The soft resin and pure resin of shellac are present in shellac as mechanical mixture since they diffuse in solution independently of each other. Pure resin of shellac has been found to be homogeneous in molecular mass as it could not be separated into fractions with different melting points and acid values, by dialysis

Alcoholic solutions of natural resins, perhaps due to their association with varnishes are often assumed to be colloidal and this idea is freely mentioned in literature without any convincing experimental support. Thus, Zsigmondy ("Chemistry of Colloids," Eng. Trans. p. 32) places resins in the class of colloids like rubber, etc. which are soluble in an organic medium. This is particularly true of shellac solutions whose colloidal nature is assumed by a number of workers including Gardner and collaborators (*Ind. Eng. Chem.*, 1929, **21**, 227; *Ind. Eng. Chem. Anal. Ed.*, 1929, **1**, 207) and Verman (Technical Paper No. 11 of London Shellac Research Bureau, pp. 4, 11) without any definite experimental evidence. Even Tschirch and Stock ("Die Harze", 1932, Band I, p. 147) are inclined to believe natural resins and their solutions as colloids and they quote the work of one of their students, Siedels, who attempts to prove the colloidal nature of resin solutions in alcohol by direct dialysis in parchment. Another observation relevant to the subject is that of Wo. Ostwald (*Trans. Faraday Soc.*, 1920-21, **16**, General Discussion, p. 89), who finds that natural resins and all other substances which spontaneously dissolve in alcohol have a perceptible rate of diffusion through collodion membranes which points to the fact that at least a part of the resin is present in true solution.

Since substances like dyes, soaps etc. which are colloidal in aqueous medium have been found out to be molecularly disperse in alcoholic solutions, it is quite probable that such solutions of natural resins may also be molecularly disperse. And the fact that most natural resins have molecular weights generally less than 2000, but usually between 300 and 700, debars them from being molecular colloids, and warrants the possibility that alcoholic solutions of the resins may be true solutions and not colloidal.

The purpose of the present paper is to investigate the nature of resin solutions in organic solvents with special reference to shellac. The problem has been investigated having regard to the following characteristic properties of colloids *viz.*, dialysis, ultrafiltration, Tyndall effect and osmotic properties.

E X P E R I M E N T A L.

Dialysis.

Investigation in alcoholic solution is rendered difficult for want of a suitable semipermeable membrane in alcoholic solution. Parchment paper is useless as being very slow in action and not perfectly wetted by alcohol, and membranes of collodion and cellophane were tried as Wo. Ostwald (*loc. cit.*) previously used them with some success in alcoholic solution. Best results were, however, obtained by using alcohol-insoluble ultra filtration membranes (commercially called ultra-cella filters) manufactured by de Haen works of Germany. The membrane was stretched across the bottom of a circular dialyser and tightly fixed there with rubber washers and suitable nuts. Dialysis was carried out with 20 c.c. of 20% dewaxed shellac solution in redistilled industrial spirit under a tightly fitting bell jar to prevent evaporation of alcohol The results with different membranes are given below.

(*a*) *Collodion Membrane.*—Both the resins present in shellac dialyse with great rapidity through such membranes and there is considerable osmosis. With 500 c.c. of alcohol as outside liquid, more than 50% of the total resin diffuse out in about 6 hours and the outside and inside concentrations equalise in about 24 hours. But the experiment is very difficult to carry out for any length of time, as the membranes swell and become soft in contact with alcohol, and in a few hours usually burst either due to osmotic rise or to slight mechanical shock.

(*b*) *Ultrafiltration Membrane.*—With ultrafilters of the grade 'ultra-cella' (finest) which is capable of retaining not only the finest gold sol but even albumins, shellac solutions in organic solvents diffuse with extreme ease. The resin may be detected in the dialysate in less than half an hour. Through a 9 cm. diameter membrane using 500 c.c. of alcohol outside and changing it once in three days, more than 50% diffuse out in the first three days and practically the whole quantity of shellac diffuses out during 4 to 5 changes That nothing colloidal is left inside after this period is shown by completely ultrafiltering the residual inside liquid through the same membrane.

(c) *Cellophane Membiane.*—With cellophane both the resins diffuse out comparatively slowly and make their presence detectable in the dialysate only after three to six hours. The slow rate is further shown by the fact that only about 20% pass through in one week.

Composition of Dialysate.

·The proportion of soft resin and pure resin present in the dialysate was determined analytically and shows the following figures for the very permeable collodion 'membrane for the first six hours, after which the membrane burst for reasons already mentioned (outside liquid—200 c.c. alcohol).

TABLE I.

Composition of dialysate during various stages of dialysis.

	Percentage of soft resin (ether soluble).	Percentage of hard resin.
Collodion membrane.		
Original shellac	29·6	70·4
0-2 hours' dialysate	52·3	47·7
2-4 hours' dialysate	50·4	49·6
4-6 hours' dialysate	47·3	52·7
' Ultra-cella ' membrane.		
Original shellac	29·6	70·4
Dialysate after 40 hours	38·7	61·3
Residue after 40 hours	18·3	81·7

The above table shows that the proportion of soft resin and hard resin continually changes in the dialysate as well as in the residual solutions. This conclusively shows that the constituents of shellac are not chemically combined but are co-existent in the solution as a mixture in approximately molecular proportion and diffuse independently, in contradiction to the idea of some previous workers (Verman and Bhattacharya, London Shellac Research Bureau Technical Paper No. 1).

Ultrafiltration.

A Zsigmondy type 9 cm. ultrafilter, modified as described below was used with 'ultracella' membranes of 'fine' and 'finest' variety. The

filter was closed with a tight fitting rubber stopper which was pressed down and kept in place by a circular brass sheet from above. The brass sheet in its turn was pressed down to the body of the filter with suitable nuts and connecting rods. The rubber cork was fitted with two glass tubes, one for connecting to a pressure gauge, while the other was connected to a pressure tubing fitted with an ordinary cycle-valve, through which air was pumped in to apply pressure. This arrangement is not only a conve- nient modification of the apparatus but is essentially necessary for use with volatile organic solvents. Otherwise. if suction is applied from below high vacuum is not created due to the high saturation pressure of the solvent; and secondly, the solvent quickly evaporates off the bottom surface of the membrane depositing a solid film of resin cn it, which hinders its further permeability. That the membranes have not ruptured during experiment was always tested with Zsigmondy's gold sol after washing the membrane with the organic solvent used and then with water. Pressure of about 25 lbs. per square inch was used. The results obtained are sum- marised below.

(a) Solutions of shellac in alcohol upto concentrations of 20% were tried and were found to pass unchanged rapidly through the finest membranes. As the concentration of shellac increases, the filtration becomes less rapid due evidently to increased viscosity. The solutions obtained on addition of water to the above solution also ultrafilters com- pletely right up to the precipitation point of shellac, if the ultrafiltration is carried out immediately. On standing fine particles of shellac separate out from the solution and remain suspended as a coarse colloid.

(b) 5% Alcoholic solutions of rosin, mastic, accroides and pontianac were tested and were found to pass completely and very rapidly through the finest ultrafilter. It is really remarkable that the pontianac solutions behave in this way, for its alcoholic solution becomes turbid on dilution with more alcohol, which is generally believed to be due to the presence of colloidal particles. But the true explanation is a different one as has been proved by the author in a previous publication (*J. Indian Chem. Soc.*, 1940, **17**, 308).

(c) Solutions of shellac (5% and 10% by weight) in aqueous acetone (10% water) were tested and were found to pass completely through the ultrafilter quite easily. Similar solution of about 20% strength also passes through the membrane but the rate is extremely slow (about 10 c.c. in 24 hours). The identity of the filtrate and the residual liquid on the filter was established by a determination of their density and refractive index.

Tyndall Effect.

The technique used was a very simple one and followed very closely to that recommended by Hatchek ('Practical Colloid Chemistry'). Carbon arc lamp was used as the light source with suitable condensing system of lenses (an epidiascope was used), and filters to cut off heat rays. The electric arc worked on a current of about 4 amperes with a drop of 110 volts, between its terminals. The solution to be tested was contained in a glass cell made of highly transparent plane glass. This arrangement was tested before use with typical colloids, e.g. Zsigmondy's gold sol, mastic sol, etc.

All the resin solutions used in the ultrafiltration experiments were tested. They were all optically void just like ordinary alcohol except the solutions which contained a large percentage of water and were close to the precipitation point. This absence of Tyndall effect is an agreement with the observations of previous workers (Bender in Alexander's "Colloid Chemistry," Vol. IV), who invariably failed to disclose the existence of colloidal particles in resin solutions by ultramicroscopic examination.

Osmotic Properties.

The osmotic properties of resin solutions in so far as freezing point depressions and boiling point elevations are concerned have been studied by many different workers to gain an idea of the molecular weights of the resins. Thus the boiling point elevation of abietic acid (the main constituent of resin) solutions in acetone has been very carefully determined recently by Bender (J. Amer. Chem Soc., 1939, 61, 1812) who has found a mean molecular weight of 378 as against the theoretical value of 302. From Tschrich and Stocks' book, it appears that a closer agreement than this is usual with most of the components of natural resins The molecular weight of shellac in alcohol has been determined in this laboratory with the Cottrell's apparatus and also elsewhere, and has been found to have an average value of 1000.

Freezing point depressions of shellac solutions in dioxane and glacial acetic acid have been studied (Palit and Bhattacharya, J. Indian Chem. Soc., 1939, 16, 258) and have always yielded values of 1000 for shellac, about 600 for soft resin (ether soluble) and 1800-2000 for pure resin (ether-insoluble). Even the fossilized copals have been found to yield an average molecular weight of 500 by cryoscopic measurements by different workers. This shows that the resin molecules are hardly associated in solution in organic solvents to form large micelles of colloidal dimension.

D I S C U S S I O N.

The position with regard to the nature of natural resin solutions has hitherto not been very clear. No systematic colloidal investigation has yet been undertaken with this end in view, but a number of molecular weight determinations by cryoscopic methods has been made in connection with the study of the individual components isolated from natural resins. In most cases, an approximate agreement with the values arrived at from chemical evidence is obtained, which shows that at least in dilute solutions these resin components form true solutions. But coming to the question of the solutions of natural resins themselves, they are almost universally supposed to be colloidal. Such an assumption rests on some indirect evidences. All resin solutions under suitable conditions of temperature and concentration are capable of forming gels which are commonly believed to be di-phasic and since solutions of resins are nothing but these gels simply with a greater proportion of solvent, a colloid structure for them is assumed as a natural corollary. Houwink's isogel concept for resins ("Natur- und Kunst-harze," 1934 ; cf. "British Plastic Year Book" 1935, p. 51) in the solid state has also materially contributed to strengthen this widespread belief for resin solutions.

The evidences presented herein, show that the assumption of colloidal nature is here totally unjustified. The idea of a reversible micellar aggregation of a part of the resin in solution, though conceivable, is not supported by osmotic evidences, as the observed molecular weights are of an order too low for micelle formation. Rapid dialysis may, however, well be explained by the micellar theory as being due to the dissociatton of micelles to the simplest units which pass through the membrane and recombine on other side, but such micelles must be extremely few in number as osmotic results show. Though a strong Tyndall effect is a positive proof of the presence of colloids, its absence, as is well known, may not be a sure indication of true solution, since the Tyndall effect depends not only on the particle size but also on the diference in refractive indices between the dispersed phase and the medium. The ultrafiltration experiment is, however, very definite in its indication and is irreconcilable with a micellar theory. For substances like soap, where micellar aggregation is definitely established, it is known from the work of McBain and Jenkins (*J. Chem. Soc.*, 1922 **121**, 2325), that only a very small portion passes through the ultrafilters as aginst the resin solutions investigated here where the whole solution passes through unchanged in composition in a few minutes. The effectiveness of these membranes, for organic solvents

has already been established by Kumichael (*Koll.-chem. Beih.*, 1928, **25**, 151', who using a cella ultrafilter obtained an ultrafiltrate of practicrlly . pure acetone from its nitrocellulose solutions. In this connection an ultrafiltration experiment quoted by Traxlar (*Chem. Rev.*, 1936, **19**, 125) is interesting. On ultrafiltering petroleum, both soft and hard asphalts dissolved in petroleum, were quantitatively retained on the ultrafilter, whereas the associated resin passes through the filter in petroleum solution. An additional proof of the non-existence of micelles or loosely bound aggregates in natural resin solutions is furnished by Houwink ("Physikalische Eigenshaften und Feinbau von Natur-und Kunstharzen," 1934,p. 206) who from viscometric investigations of such solutions arrived at the same conclusion. It seems, therefore, highly probable that resin solutions are non-colloidal in spite of their great gel-forming capacities. Of course, gel-forming tendency is not necessarily associated with a colloidal structure as proved in the case of alcoholic solutions of soaps (*vide*, Lederer, "Kollo d Chemie der Seifen," 1932, pp. 78, 229) or linseeed oil, pure or moderate y oxidised, which according to Freundlich (*J. Oil & Colour Chem. Assoc*, 1935, **18**, 74) is non-colloidal since its benzene solution easily passes through the ultrafilter.

For shellac it has sometimes been postulated (Bhattacharya ard Gidvani, London Shellac Research Bureau, Technical Paper No. 16) that it is composed of all sorts of polymers ranging from 300 to 3,000 in molecular weight. Our experiences have always been to the contrary so far as diffusion experiments are concerned. In one of our experiments pure resin solution in alcohol was dialysed in the finest ultrafilter membrane. The dialystates at different stages of dialysis and also the residue were compared with one another and were found to be identical in acid values and melting points within the limits of experimental error. If pure resin were composed of molecules differing widely in molecular weights, we could reasonably expect to effect some segregation of heavy and light molecules by dialysis with consequent difference in melting points and acid values of these fractions.

The absence of all typical and fundamental colloidal properties in resin solutions *e.g.*, low rate of diffusion, negligible lowering of vapour pressure, Tyndall effect and retention on ultrafilters, makes it imperative to explain the so-called colloidal properties of resin solutions *e g.*, high viscosity, tendency towards gel formation, characteristic tackiness, etc., on solvation basis. There is no doubt that solvation is an essential phenomenon in such solutions but the inadequate nature of our knowledge of solvation stands in our way to any fruitful discussion on the point. It seems that Stewart's conception

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(*Chem. Rev.*, 1929, **6**, 483 ; *Trans. Faraday Soc.*, 1937, **33**, 239) of ' cybotactic groups ' or evanescent swarms may be nearer to truth for such solution, a view advocated by Bender (*loc. cit.*) who brings out some experimental evidence in its support.

The important question now arises whether resin solutions should be regarded as systems in thermodynamic equilibrium or not. In other words, we are to answer the question, given the temperature and concentration of the system, are all other properties definite and invariable for such a system? We must admit that at the present state of our knowledge an unequivocal answer is not available. For intrinsic colloids like high-molecular-weight synthetic resins, it is the general experience that the properties of the resin solutions depend to some extent on the past history of the same but in not such a remarkable manner as the aqueous solutions of gelatin, albumen, etc. This is clearly brought out by the cryoscopic measurements of Bender (*loc. cit.*) on solutions of rosin and some phenolic resins where he finds a considerable difference in the boiling point elevations of similar solutions prepared in slightly different manner. The same worker finds that the viscosity of resin solutions changes slowly with time. It appears, therefore, that the properties of such solutions are not defined completely by two parameters but have some degree of latitude within short limits, which in its turn depends on the structural complexity of the resin and its affinity for the solvent. Recently, however, Papkov and co-workers (*Acta Physicochem.*, 1938, **3**, 647) have found out that in the dissolved state of highly polymerised substance, molecular dispersions are obtained, and the phase rule is completely applicable to the system, highly polymerised substance-solvent.

MECHANISM OF MUTAROTATION OF
D-OXYMETHYLENE CAMPHOR.

By W. V. Bhagwat, S. Harmalkar and S. S. Deshapande.

Mutarotation of d-oxymethylenecamphor has been examined with reference to its fractional change in rotation (when it becomes constant) being independent of initial concentration. Results on the velocity of mutarotation from copper salt indicate that the mutarotation consists in the transformation of enol into keto form.

Pope and Read (*J. Chem. Soc.*, 1909, **94**, 176) and Bishop, Claisen and Sinclair (*Annalen*, 1894, **281**, 331) have observed that d-oxymethylene-camphor shows a change in optical rotation with respect to time, both in benzene and alcohol. The results in alcohol refer to one concentration only, while in benzene they have studied the change for three concentrations.

Pope and Read (*loc. cit.*) have not shown that fractional change in rotation, when it has become constant, is independant of initial concentration, a condition necessary for mutarotation. We have, therefore, examined the question and our results in absolute ethyl alcohol are given below.

TABLE I.

Wt. of the substance.	Length of the tube.	Time.	a_D.	a_∞/a_0.
2·454 (g. /100 c.c.)	1 d. cm.	0 hr.	4·85	0·928
,,		26	4·50	
2·518		0	5·00	0·930
,,		26	4·65	
1·878		0	3·70	0·932
,,		20	3·45	
5·767		0	11·2	0·941
,,		48	10·55	
1·280		0	2·50	0·920
,,		24	2·30	
6·183		0	12·0	0·933
,,		48	11·2	
2·8616	2 d.cm	0	10·45	0·938
,,		24	9·80	
1·6584		0	6·4	0·937
,,		24	6·9	

The above results, therefore, indicate that d-oxymethylenecamphor shows mutarotation.

Although Pope and Read (*loc. cit.*) have observed the optical rotation of d-oxymethylenecamphor to change with time, no attempt so far has been made to study the rate of this change   Our results in ethyl alcohol with and without HCl as catalyst are recorded below.

. In determining the order of the reaction, the difference between the constant reading (a_∞) and reading at any time t, is taken to be proportional to the concentration of d-oxymethylenecamphor at that time and is there·fore $= a - x$, where 'a' is the initial concentration when $t = 0$.

TABLE II.

. Wt. of the substance $= 5 \cdot 757$ g. in 100 c.c. a_D is in 1 d.cm. tube. Temp $= 24 \cdot 5°$.

t.	a_D.	$a - x$.	$K_1 = \frac{1}{t} \log \frac{a}{a-x}$.	t.	a_D.	$a - x$.	$K_1 = \frac{1}{t} \log \frac{a}{a-x}$.
0 min.	11·2	0·65 (a)		135 min.	10·80	0·25	0·00706
30	11·1	0·55	0·00557	210	10 70	0·15	0·00697
55	11·0	0·45	0·00667	275	10·65	0·10	0·00686
80	10·90	0·35	0·00773	∞	10·55	...	
100	10·85	0·30	0·00771				

TABLE III.

Wt. of the substance $= 6 \cdot 183$ g. in 100 c. c. a_D is in 1 d.cm. tube. Temp. $= 25° 5$.

t.	a_D.	$a - x$.	$K_1 = \frac{1}{t} \log \frac{a}{a-x}$	t.	a_D.	$a - x$.	$K_1 = \frac{1}{t} \log \frac{a}{a-x}$.
0 min.	12·0	0 80 (a)		91 min.	11·60	0·40	0·00759
15	11·90	0·70	0·00888	108	11·55	0·35	0 00764
35	11·80	0·60	0·00821	134	11·50	0·30	0·00731
50	11·75	0·55	0·00745	155	11·45	0·25	0·00750
60	11·70	0·50	0·00782	195	11·40	0·20	0·00708
76	11·65	0·45	0·00757	450	11·25	0·05	0·00614
				∞	11·20	,,,	,,.

TABLE IV.

Wt. of the substance $= 3\cdot6500$ g. in 100 c.c. $0\cdot2$ C.c. of $2\cdot117N$-HCl were added. Temp. $= 24°$. a_D is in 2 d.cm. tube.

$t.$	a_D.	$a-x$.	$K_1 = \dfrac{1}{t} \log \dfrac{a}{a-x}$.
0 min.	13·25	1·40 (a)	...
35	12·80	0·95	0·0110
190	12·05	0·20	0·0101
225	12·00	0·15	0·0099
260	11·85	...	...

TABLE V.

Wt. of the substance $= 2\cdot1896$ g. in 100 c.c. $0\cdot2$ C.c. of $2\cdot117N$-HCl added. Temp. $= 20\cdot7°$. a_D is in 2 d.cm. tube.

$t.$	a_D.	$a-x$.	$K_1 = \dfrac{1}{t} \log \dfrac{a}{a-x}$.	$t.$	a_D.	$a-x$.	$K_1 = \dfrac{1}{t} \log \dfrac{a}{a-x}$.
0 min.	8·30	1·40 (a)	...	162 min.	7·60	0·70	0·00414
18	8·20	1·30	0.00414	190	7·50	0·60	0·00437
37	8·05	1·15	0·00529	232	7·40	0·50	0·00437
49	8·00	1·10	0·00483	254	7·35	0·45	0·00437
63	7·95	1·05	0·00460	284	7·30	0·40	0·00437
78	7·90	1·00	0·00437	438	7·05	0·15	0·00506
92	7·80	0·90	0·00483	476	7·05	0·15	0·00460
108	7·75	0·85	0·00460	501	6·95	0·05	0·00667
127	7·70	0·80	0·00437	∞	6·90	...	...

Estimation of the enolic Form.

Attempts were made by us to see whether ordinary d-oxymethylene-camphor exists mainly in its keto or enol form. Enol form of the compound, as it contains OH group in the side-chain, should behave as an acid, and hence could be titrated with sodium hydroxide. The amount of alkali required is therefore a direct measure of the amount of enolic form in the given amount of the compound, provided no change occurs during titration.

The other method that was employed for this keto-enol estimation is due to Heiber (*Ber*, 1921, **54**, 902). We modified the method as follows.

Instead of adding copper acetate solution in alcohol-chloroform mixture, aqueous copper acetate was added to the substance dissolved in alcohol. The precipitate of copper salt formed was then extracted with choloform and the chloroformic solution was then decomposed by dilute sulphuric acid. The copper thus liberated was then estimated volumetrically.

TABLE VI.

Estimation of enol form by NaOH titration.

d-Oxymethylenecamphor. Wt. taken	Wt. calc.	Enol %.	Vol. of NaOH. (0·0303N)
0·1913g.	0·1848g.	96·6	33·90 c.c.
0·1714	0·1608	94·4	29·50
0·1600	0·1567	97·9	28·75
0·1830	0·1820	99·4	33·40

It seems therefore that *d*-oxymethylenecamphor exists mainly as an enol, although it is not unlikely that addition of alkali might be converting the keto form into enol form.

TABLE VII.

Estimation of enol by forming copper salt, (Heiber's method). 0·02658N-thiosulphate used for titration.

Wt. of substance.	Vol required (Cu salt).	Wt of substance calc.	Enol %.
0·0918g.	8·3 c c.	0·07941g	86·5
0·1458	12·3	0·11770	80·7
0·2083	18·0	0·17220	82·6
0·6033	—	0·49500	82·5
0·1180	—	0·09710	82·3
0·3170	—	0·26020	82·0
0·2362	—	0·19410	82·2
0·0568	—	0·04670	82·0

These results confirm that *d*-oxymethylenecamphor mainly exists in enolic form, the percentage of enol being about 80.

Velocity of Mutarotation of d-Oxymethylenecamphor.

A known weight of the substance was dissolved in a known volume of absolute alcohol. A known concentration of catalyst (HCl) was added and the amount of enol was estimated in terms of thiosulphate required for a definite volume of solution taken out from time to time. The results are as follows.

TABLE VIII.

1·4123 G. of substance dissolved in 50 c. c. of absolute alcohol. 0·2 c. c. 2·117N-HCl added, 5 c. c. of the solution titrated at a time against 0·2776N-thiosulphate solution. Temp.=23·8°.

t.	Thio required.	Enol %.	$K_1 = \frac{1}{t} \log \frac{a}{a-x}$.
0 min·	13·5 c. c.	95·5%	
65	12·2	85·6	0·00159
120	11·7	82·7	0·00120
180	11·4	81·3	0·00094
24 hours	11·1	78·5	0·000133

It is clear from above that the reaction is not unimolecular.

TABLE IX.

0·8382 G. of the substance dissolved in 50 c. c. of alcohol. Temp. 43·8°. Conc. of HCl same as above.

t.	Thio required.	Enol %.	$K_1 = \frac{1}{t} \log \frac{a}{a-x}$.
0 min	7·2 c. c.	85·8	
30	6·0	71·5	0·00607
60	5·0	59·6	0·00607
90	4·25	50·6	0·00589
120	3·85	45·9	0·00520
150	3·30	39·3	0·00518
180	3·15	37·5	0·00455
21 hours	2·40	29·2	

The velocity coefficients slowly fall with increase of time.

DISCUSSION.

The results of keto-enol estimation by Heiber method (*loc. cit.*) and by titration with alkali clearly establish the fact that *d*-oxymethylene-camphor mainly exists in the enolic form. This view confirms the observation of Brühl (*Z. physikal. Chem.*, 1900,**34**, 1), Federlin (*Annalen*, 1907, **356**, 251) and of Pope and Read (*J. Chem. Soc.*, 1909, **94**, 176) made by refractometric, calorimetric and polarimetric methods respectively. Brühl (*loc. cit.*) and Federlin (*loc. cit.*) suggested that the constitution of *d*-oxymethylenecamphor is represented as

$$C_8H_{14} \diagdown \begin{matrix} C:CHOH \\ | \\ CO \end{matrix}$$

Pope and Read (*loc. cit.*) have criticised the work on the ground that these workers have not considered the possibility of the formation of equilibrium mixture of two enolic modifications suggested by Claisen (*Annalen*, 1894, **281**, 306).

$$C_8H_{14} \diagdown \begin{matrix} C:CHOH \\ | \\ CO \end{matrix} \rightleftharpoons C_8H_{14} \diagdown \begin{matrix} C \cdot CH:O \\ \| \\ C \cdot OH \end{matrix}$$

Type (I)

They have come to the conclusion that *d*-oxymethylenecamphor shows mutarotation due to this change of one enolic form into another. Our results with velocity of mutarotation as investigated by copper salt method clearly point out that the amount of enol decreases with time; and since it is the only the enol which can form copper salt, this decrease clearly indicates that muta change consists in the transformation of enol into keto form.

$$C_8H_{14} \diagdown \begin{matrix} C:CHOH \\ | \\ CO \end{matrix} \rightarrow C_8H_{14} \diagdown \begin{matrix} CH \cdot CH:O \\ | \\ CO \end{matrix}$$

Type (II)

Pope and Read (*loc. cit.*) have offered no experimental support to their suggestion except the work of Brühl (*loc. cit.*) and Federlin (*loc. cit.*) which in reality does not exclude the possibility of keto change during mutarotation. Moreover, Pope and Read did not show that the ratio of final rotation to initial rotation is constant whatever may be the initial concentration of the substance However, our polarimetric results

show that ratio of the final rotation to initial rotation is constant and is independent of initial concentration. But this constancy need not necessarily confirm the view of Pope and Read for, even in case of equilibrium of the type (II), similar results are possible. Study of muta-rotation by polarimeter is therefore not enough to draw any conclusion since both constitutions are admissible. The investigation by copper salt method for enolic form therefore is the only way to decide between the two possibilities. The fact that the amount of enol decreases with time clearly confirms our suggestion that in mutarotation, enol changes to the keto form. If both forms are enolic the weight of copper salt formed with time should have remained constant.

There is no doubt therefore that mutarotation involves a change from enol to keto from (Type II). This change may be either an equilibrium change or one-sided.

The constancy of the ratio of initial rotation to final rotation cannot decide between these possibilities, since whether the change is complete or fractional, in this case change being from one molecule to one molecule the ratio must come out to be a constant. Results with copper salt method, however, support the equilibrium view. For if the reaction is one-sided all enol will become keto at the end and no copper salt will be formed. This, however, is not observed. When the concentration of the enol form has fallen to a certain extent there is no further change.

The change associated with mutarotation cannot be of such a simple type. In that case the calculation of velocity constants by the formulae

$$K_1 = \frac{1}{t} \log \frac{a}{a-x}$$

should not give constant results. Actually polarimetric results give a constant value for velocity coefficient and also for the ratio of final rotation to the initial rotation. However, the monomolecular formula fails when results are expressed in terms of copper salt. It is clear therefore that mutarotation change also involves a side reaction in such a way that the ratio of mutarotation values is not affected.

It seems likely that the mechanism of mutarotational change can be correctly represented as :

$$C_8H_{14} \left\langle \begin{matrix} C:CHOH \\ | \\ CO \end{matrix} \right. \quad \rightarrow \quad C_8H_{14} \left\langle \begin{matrix} C.CH:O \\ \| \\ COH \end{matrix} \right. \quad \rightleftharpoons \quad C_8H_{14} \left\langle \begin{matrix} CH \cdot CH:O \\ | \\ CO \end{matrix} \right.$$

$$\text{(A)} \qquad\qquad\qquad \text{(B)} \qquad\qquad\qquad \text{(C)}$$

At first the enolic form (A) changes into the second enolic form (B) which then forms an equilibrium with (C). It is likely that the form B and

C have practically the same optical rotation so that for all calculations by polarimeter the change is only represented by A $\longrightarrow$ B which is mono-molecular reaction. This is why the polarimetric results give more or less a constant value with the formulae $\frac{1}{t} \log \frac{a}{a-x}$ and also for the ratio of the initial rotation to the final rotation. But for copper salt method both A and B form copper salts while C does not, and hence the change cannot be represented only as A$\longrightarrow$B and monomolecular constant is therefore not possible.

Let us consider the above change

$$A \longrightarrow B \rightleftharpoons C$$
$$\text{Hydroxy (i)} \quad \text{Hydroxy (ii)} \quad \text{Keto.}$$

Let the initial concentration of Hydroxy (i) be ' a ' and its concentration at any time t, be $a-x$ then for the reaction A$\longrightarrow$B, we have

$$\frac{dx}{dt} = K_1 (a-x) \qquad \qquad \dots (i)$$

Let the concentration of B and C at the same time, be m and y ; then for the reaction B$\longrightarrow$C $\frac{m}{y} = K$ or $m = Ky$ $\qquad \dots (ii)$

But the total concentration at all times must be $= a$, the initial concentration. Hence

$$a = a - x + m + y = a - x + Ky + y = a - x + y (1 + K)$$
or $$x = (1 + K)y \qquad \qquad \dots (iii)$$

Substituting the value of x in equation (i) we get

$$\frac{dx}{dt} = K_1 \left\{ a - (1+K) y \right\} = K_1 (1+K) \left\{ \frac{a}{1+K} - y \right\}.$$

Putting $K_1 (1+K) = K_2$ and $\frac{a}{1+K} = b$ we get

$$\frac{dx}{dt} = K_2 (b-y) \quad \dots (iv)$$

but $$x = (1+K) y \text{ or } dx = (1+K) dy$$

Hence $$(1+K)\frac{dy}{dt} = K_1 (1+K) (b-y)$$

or $$\frac{dy}{dt} = K_1 (b-y) \text{ or } K_1 = \frac{1}{t} \log \frac{b}{b-y}. \qquad \dots (v)$$

Since initially *d*-oxymethylenecamphor is mainly enolic, there is no B or C. Also when value of copper salt becomes constant with time there is no A and whole is $B + C = a$. The change from A→B does not change the weight of copper salt; hence any change in its amount with respect to time must be due the formation of C. Thus we get y or concentration of C at any time. When there is no further fall in the weight of copper salt the weight corresponds to the weight of B at equilibrium. Knowing the corresponding amount of C we get $K = m/y$. a is known, hence $b = a/1 + K$ can be calculated. Thus the above equation and hence the mechanism of mutarotation can be verified. Our results are as follows :

TABLE X.

$1\cdot4123$ G. of the *d*-oxymethylenecamphor dissolved in 50 c.c. of alcohol. $0\cdot2$ c.c. of $2.117N$ HCl added. Temp. $= 23.8°$. 5 c.c. of the solution were titrated with $0\cdot02776N$ thiosulphate.

$t.$	Thio.	$y.$	$K.$	$b.$	$b—y.$	$K_1 = \frac{1}{t} \log \frac{b}{b—y}.$
0 min.	13·5 c.c.	—	11.1/2.4	—	—	
65	12·2	1·3	$=4.625$		1·1	0·0120
120	11·7	1·8	...	$\frac{13\cdot5}{5\cdot625}$	0·6	0·0115
180	11·4	2·1	...	$=2.4$	0·3	0·0115
24 hours	11·1	2·4	...	...	—	...

TABLE XI.

$0\cdot8382$ G. of *d*-oxymethylenecamphor dissolved in 50 c.c. of alcohol. $0\cdot2$ C.cs. of $2.117N$-HCl added. Temp. $= 33.8°$. 25 C.c. of solution were titrated with $0\cdot02776N$-thiosulphate.

4

t.	Vol. of thio	y.	K.	b.	$b-y$	$K_1 = \frac{1}{t} \log \frac{b}{c-y}$
o min	7·2	—	0·5	$\frac{7\ 2}{1+0.5}$	...	
30	6·0	1·2	...	=4.8	3.6	0.00957
60	5·0	2·2	...	...	2.6	0.0103
90	4·25	2·95	...	...	1.85	0.0106
120	3·85	3·35	...	...	1.45	0.00996
150	3·30	3·90	...	...	0.90	0.0110
180	3·15	4·05	...	...	0.75	0.0101
21 hours	2·40	4·80	...	...	...	...

The consistency of the velocity constants clearly confirms the above view about the mechanism of muta-rotational change of d-oxymethylene camphor.

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DETERMINATION OF THE SPACE GROUP OF THE CRYSTALS OF O-, M- AND P- NITROBENZOIC ACIDS.

BY V. C. THAKAR, M. R. KAPADIA AND MATA PRASAD.

Crystallographic measurements of o-, m- and p-nitrobenzoic acids have been made and their space groups affixed

In the study of these crystals K_a radiations from a copper anti-cathode were used. The rotation photographs and oscillation photographs at an interval of $15°$ or $10°$ about the principal axes of the crystals, were taken by means of Bernal's photogoniometer and the latter were interpreted by means of Bernal's chart.

o-Nitrobenzoic Acid.

The crystals of o-nitrobenzoic acid are found to develop the following faces :

$$a(100), \ b'(0\bar{1}0), \ m(110) \ \text{and} \ c(001).$$

They belong to the triclinic pinacoidal class and the values of a, β and γ and the axial ratio, calculated by Steinmetz from the crystallographic measurements in two different ways are :

I. $a = 131°·11\frac{1}{2}', \quad \beta = 109°·37', \quad \gamma = 61°·54\frac{1}{2}';$
         $a : b : c = 0·5364 : 1 : 0·3576.$

II. $a = 48°·48\frac{1}{2}', \quad \beta = 61°·54\frac{1}{2}', \quad \gamma = 109°·37';$
         $a : b : c = 1·5098 : 1 : 2·7963.$

(*cf.* Groth, "Chemische Krystallographie", Vol. IV, p. 472).

Crystals of the substance were obtained from dilute alcohol but it was found that the same type of crystals can be obtained from a solution of the substance in distilled water.

The lengths of the axes determined from the rotation photographs (Plate I, Fig. 1—3) about a, b and c axes are : $a = 7·58\text{Å}$, $b = 14·01\text{Å}$, $c = 5·05$ Å.

These rotation photographs were obtained when the setting of the crystal was done with values of a, β and γ, given in the first data. These lengths give an axial ratio $a : b : c = 0·541 : 1 : 0·361$, which is in good agreement with the first data of Steinmetz.

The list of reflecting planes in the crystal along with their approximate relative intensities is given in Tables I and II.

It appears from these data that there are no abnormal halvings. The crystals, therefore, belong to the space group C_i^1 which requires two asymmetric molecules for the unit cell. The number of molecules calculated from the dimensions of the unit cell and the density of the crystals which was found to be 1·559 is also 2. This shows that one chemical molecule of the substance represents the asymmetric unit of the unit cell.

The ratio of the axes given in the second data of Steinmetz can be obtained from the lengths of the axes obtained above if the b and c axes are interchanged. This interchange was done by Steinmetz with a view to obtain a high value for the parameter ω because the corresponding value for the crystal of benzoic acid is also high. But the value of α in the second data is the supplement of the value of α in the first data and consequently the number of molecules in the unit cell calculated from the second data comes out to be 0·46 which is absurd. Also it has been found impossible to interpret the oscillation photographs with the values of α, β and γ given in the second data. These observations, therefore, establish that the first crystallographic data is the correct one.

<p align="center">m-<i>Nitrobenzoic Acid (stable modification)</i>.</p>

Crystals of the substance obtained from alcohol or water are found to develop the c(oo1) and q(o11) faces. They belong to the monoclinic prismatic class and the axial ratio obtained from the crystallographic measurements is $a : b : c = $0·9656 : 1 : 1·2326 and $\beta = $91°·11½′
(*cf.* Groth, *ibid*, p. 475).

The lengths of the axes calculated from the rotation photographs (Plate II, FIG. 1—3) about the principal axes are

$$a = 10.41\text{Å}, \quad b = 10.69 \text{ Å}, \quad c = 13.22\text{Å}.$$

These give the axial ratio $a : b : c = $0·973 : 1 : 1·236 which is in good agreement with that given above.

The list of reflecting planes in the crystal with their approximate relative intensities is given in Tables III and IV which show that the planes (hol) are halved when h is odd and (o1o) is also halved. The crystal, therefore, belongs to the space group C_{2h}^5 which requires four asymmetric molecules in the unit cell. The number of molecules calculated from the dimensions of the unit cell and the density of the crystal which was found to be 1·527, is 8 (accurately 8·11). This leads to the conclusion that two molecules of m-nitrobenzoic acid associate together to form one asymmetric unit present in the unit cell.
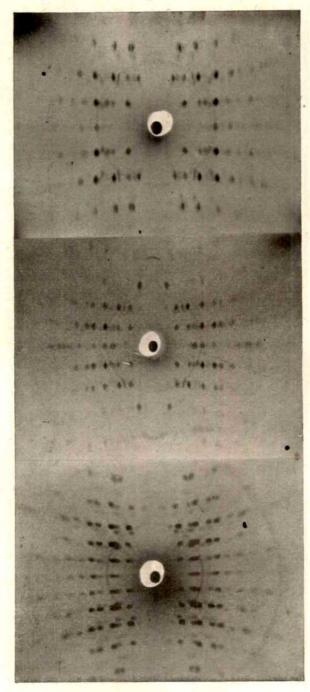
A remarkable feature of the oscillation photographs about a and c axes is that the intensities of spots corresponding to (hkl) planes was very

PLATE II.

Rotation photographs of m-nitrobenzoic acid.

FIG. 1.

a-axis
$D = 5.00$ cm.

FIG. 2.

b-axis
$D = 4.00$ cm.

FIG. 3.

c-axis
$D = 4.00$ cm.
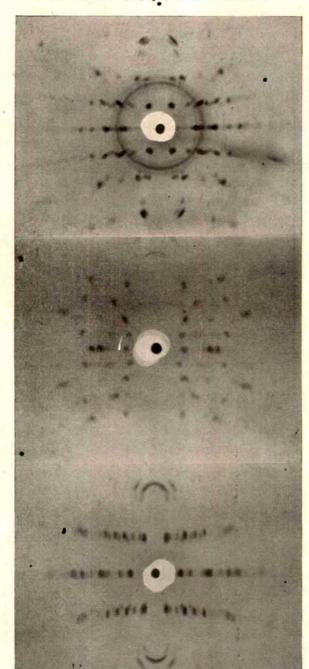
PLATE I.

Rotation photographs of o-nitrobenzoic acid.

FIG. 1.

a-axis
$D = 3.50$ cm.

FIG. 2.

b-axis
$D = 4.00$ cm.

FIG. 3.

c-axis
$D = 3.60$ cm.

different from that of (hkl), although the angle β is equal to $91°\cdot11\frac{1}{4}'$. This is usually not observed in monoclinic crystals in which the angle differs slightly from $90°$.

A note on the results of this crystal (*Current Sci.*, 1938, **6**, 44 was published by one of the authors (V. C. T.) in which through mistake the number of molecules in the unit cell has been given incorrectly as 4.

p-*Nitrobenzoic Acid.*

The crystals of the substance have been found to develop the following faces:

$$c(001), \quad r(10\bar{1}), \quad \rho(10\bar{1}), \quad a(100), \quad q(011) \text{ and } w(11\bar{1}).$$

They belong to the monoclinic prismatic class and the axial ratio found by crystallographic measurements is

$$a : b : c = 2\cdot5615 : 1 : 4\cdot2314 \text{ and } \beta = 96°\cdot38 \text{ (} cf. \text{ Groth, } ibid., \text{ p. 477)}.$$

TABLE I.

Axial planes.		okl.		hol.		Prism planes hko.		hko. (contc.)	
001	v. s.	011	v. s.	10$\bar{1}$	s.	110	v. s.	1$\bar{1}$0	s.
002	v. w.	012	m.	102	w.	120	m.	1$\bar{2}$0	m. s.
010	w. m.	021	w.	20$\bar{1}$	m. s.	1$\bar{3}$0	s.	1$\bar{3}$0	v. s.
020	s.	031	v. w.	30$\bar{1}$	m.	140	m. s.	1$\bar{4}$0	m. s , m.
030	m. s., s.	01$\bar{1}$	v. s.	10$\bar{1}$	s.	150	w.	1$\bar{5}$0	v. w.
040	s.	01$\bar{2}$	w.	10$\bar{2}$	w.	210	m. s.	2$\bar{1}$0	m. s.
100	v. s., s.	021	m.	20$\bar{1}$	w. m.	220	s.	2$\bar{2}$0	m. s.
200	s.	02$\bar{2}$	m.	20$\bar{2}$	m.	230	w. m.	2$\bar{3}$0	m. s., m.
300	s.	03$\bar{1}$	m. s.	30$\bar{1}$	w. m.	240	w. m.	2$\bar{4}$0	w. m.
		03$\bar{2}$	m. s.			260	w. m.	310	m.
		04$\bar{1}$	v. s.			310	m. s., m.	3$\bar{2}$0	m.
		04$\bar{2}$	w. m.			320	s.	3$\bar{3}$0	w.
		05$\bar{1}$	m.			330	w. m.	3$\bar{4}$0	m. s.
		052	w. m.			340	m. s.		
		06$\bar{1}$	w. m.			410 }	w.		
		06$\bar{2}$	m.			420 }			
		07$\bar{1}$	w.						
		07$\bar{2}$	v. w.						

TABLE II.

General planes

111 v. w.	12$\bar{2}$ m.	211 w.	22$\bar{2}$ w. m.	311 m.	37$\bar{2}$ m.
121 m.	13$\bar{1}$ s.	221 v. w.	23$\bar{1}$ m. s.	31$\bar{1}$ m.	311$\bar{}$ v. w.
$\bar{1}$22 m. s.	13$\bar{2}$ w. m.	231 m.	23$\bar{2}$ w.	32$\bar{1}$ w.	$\overline{32}$1 w.
131 w. m.	14$\bar{1}$ v. s., s.	2$\bar{1}$1 m. s.	24$\bar{1}$ w. m.	33$\bar{1}$ w. m.	$\overline{33}$1 w.
$\bar{1}\bar{1}$1 m. s., m.	14$\bar{2}$ w. m.	22$\bar{1}$ m.	24$\bar{2}$ m. s.	34$\bar{1}$ m. s.	44$\bar{1}$ m. s.
121 m. s., m.	14$\bar{3}$ w. m	222 w. m.	24$\bar{3}$ w	35$\bar{1}$ w.	43$\bar{1}$ w. m.
122 w.	15$\bar{1}$ m. s.	23$\bar{1}$ s.	25$\bar{1}$ w.	3$\bar{1}$1 w.	44$\bar{1}$ m. s
13$\bar{1}$ m.	15$\bar{2}$ m. s.	23$\bar{2}$ w. m.	25$\bar{2}$ m.	32$\bar{1}$ m.	44$\bar{2}$ m. s.
$\bar{1}$32 m.	16$\bar{1}$ w.	24$\bar{1}$ w. m.	26$\bar{1}$ m.	33$\bar{1}$ w.	45$\bar{1}$ m. s.
1$\bar{4}$1 m.	16$\bar{2}$ w. m.	24$\bar{2}$ w. m.	27$\bar{2}$ w. m.	33$\bar{2}$ w.	
1$\bar{4}$2 w. m.	17$\bar{1}$ v. w.	25$\bar{1}$ w. m.	28$\bar{2}$ m. s.	34$\bar{1}$ m. s.	
152 m.	17$\bar{2}$ w. m.	2$\bar{5}$2 w.	2$\bar{1}\bar{1}$ m.	34$\bar{2}$ v. w.	
162 m. s.	$\bar{1}\bar{1}$1 w.	2$\bar{6}$2 w. m.	23$\bar{1}$ w. m.	35$\bar{1}$ w. m.	
111 m. s.	1$\bar{1}\bar{2}$ m.	2$\bar{1}\bar{1}$ m.		36$\bar{1}$ w. m.	
11$\bar{2}$ w. m.	1$\bar{2}\bar{1}$ w. m.	21$\bar{2}$ w. m., m.		37$\bar{1}$ w. m.	
12$\bar{1}$ s.	1$\bar{3}\bar{1}$ w. m.	2$\bar{2}$1 m. s.			

TABLE III.

Axial planes.		Prism p l a n e s		
okl	okl (contd.)	okl (contd.)	hol.	hko.
001 w. m.	011 w. m.	036 m.	201 m. s.	120 w.
002 w. m.	012 v. w.	041 m.	202 v. w.	130 s.
003 w. m., w.	013 w. m., m.	042 w. m.	203 s.	140 w.
004 w.	014 w. m.	043 w. m., m.	204 m. s., m.	210 m. s.
005 w.	015 w.	044 w.	205 w.	220 v. w.
006 w.	017 w m.	051 w. m.	206 w. m.	230 m.
007 v w.	021 w. m.	052 w.	2$\bar{0}$1 v. s.	240 w. m.
020 w. m.	022 m. s.	053 w. m.	20$\bar{2}$ s.	310 v. w.

Table III (contd.).

Axial planes.	Prism planes		
	okl.	hol.	hko.
040 m.	023 m., m. s.	$20\bar{3}$ w. m$_s$	320 w. m.
200 m.	024 w.	$20\bar{5}$ m. s.	330 w.
400 w. m.	026 v. w$_s$	$20\bar{6}$ w. m.	340 w.
	027 w.	401 w., w. m$_s$	420 w.
	031 w. m., m.	402 m.	430 w.
	032 w.	403 m$_s$	440 m., w. m.
	033 w.	404 w$_s$ m.	530 w.
	034 w. m., m.	$40\bar{1}$ m$_s$	
	035 w. m.	$40\bar{2}$ m. s$_?$	
	054 w.	$40\bar{3}$ m. s., m.	

Table IV.

General planes.

111 v. s.	134 w.	224 m. s.	311 s., m. s.	411 m. s., m.
112 m.	$\bar{1}35$ m. s., m.	227 w. m.	312 v. s., s.	412 m.
113 s.	$13\bar{6}$ v. w.	$22\bar{1}$ v. w.	313 s.	413 m.
114 m.	$14\bar{1}$ v. w.	$22\bar{2}$ w. m.	314 m. s., m.	414 m.
116 w. m.	$14\bar{2}$ w. m.	$22\bar{3}$ w. m.	315 w.	$41\bar{1}$ w. m.
$11\bar{1}$ w.	$14\bar{3}$ w. m.	$22\bar{4}$ m.	$31\bar{1}$ s.	$41\bar{2}$ w. m.
$11\bar{2}$ m. s.	151 w.	$22\bar{5}$ w. m.	$31\bar{3}$ m.	$41\bar{3}$ m.
$11\bar{3}$ w. m., m.	152 v. w.	231 m.	$31\bar{4}$ w. m.	$41\bar{5}$ m.
$11\bar{4}$ w. m.	153 v. w.	233 w. m.	$31\bar{5}$ w. m.	421 w. m.
$11\bar{5}$ w.	$15\bar{1}$ v. w.	234 v. w.	$31\bar{6}$ w. m.	422 m. s., m.
$11\bar{6}$ w. m.	$15\bar{2}$ w. m	235 w. m.	324 v. w.	423 m.
121 v. s.	$15\bar{3}$ w. m.	236 v. w.	325 v. w.	424 w.
122 s.		$23\bar{1}$ m.	$32\bar{1}$ w. m.	425 w. m.
123 m.		$23\bar{2}$ v. w.	$32\bar{2}$ v. w.	426 w.
124 m.		$23\bar{4}$ w.	$32\bar{3}$ m.	$42\bar{1}$ w. m.

TABLE IV (contd.).

General planes.

	211 m. s., m.			
125 w., v. w	212 v. s.	241 v. w.	$32\bar4$ w m.	$42\bar2$ w.
127 w.	213 v. s., s.	243 v. w.	333 w.	$42\bar5$ m.
$12\bar1$ w. m.	214 w. m.	245 v. w.	334 m.	431 w. m.
$12\bar2$ w.	215 w. m., m.		335 v. w.	432 m., w. m.
$12\bar4$ m.	$21\bar1$ m. s., m.	$24\bar1$ v. w.	$33\bar1$ v. w.	433 w. m.
$12\bar7$ w.	$21\bar2$ w. m.	$24\bar2$ m.	$33\bar2$ w. m.	434 w. m.
$13\bar2$ m.	$21\bar3$ w. m.	$24\bar3$ w. m.	$34\bar1$ w. m.	435 m.
133 m.	$21\bar4$ m.	$25\bar1$ v. w.	$34\bar2$ v. w.	$43\bar1$ w. m.
134 w. m., m.	$21\bar5$ m., m. s.	$25\bar2$ v. w.	343 w.	$43\bar2$ w m.
135 w. m.	$21\bar6$ w. m.	$25\bar3$ w. m.	344 w. m.	$43\bar3$ w.
136 w.	$21\bar7$ w.		345 w. m.	$44\bar2$ w. m., w.
$13\bar1$ m.	221 m.		$34\bar1$ m. s.	$44\bar3$ m.
$13\bar2$ w.	222 s.		$34\bar2$ v. w.	511 w.
	223 m. s.		343 v. w.	513 v. w.
			351 v. w.	511 w.
				$51\bar3$ w., v. w.
				$52\bar1$ w.
				$5\bar22$ v. w.
				$53\bar1$ w.

TABLE V.

Axial planes.	Prism planes			
	okl	hol	hol	hko
1	2	3	4	5
002 m. s., m.	011 w. m.	202 v. s.	404 s.	120 s.
008 w. m.	012 w. m.	20(10) m. s.	$40\bar6$ w.	210 w. m.
020 m	013 w. m., m.	$20\bar2$ m., w. m.	$40\bar8$ w. m., m.	220 w. m.
200 v. s.	015 v. s., s.	$20\bar4$ w. m.	604 w. m.	320 w., w. m.
600 w. m.	017 w.	$20\bar6$ w. m., m.	600 } w. m.	420 w.
	019 v. w.	$20\overline{10}$ m_s	$60\bar2$ }	510 m_s

TABLE V.-(contd.).

Axial planes.			Prism planes.	
okl.	**hol**			
022 w.	402 m.	604̄ m.		520 w. m.
024• m., w. m.	404 m. s.			
025 w. m.	408 w	606̄ m.		
026 w. m.	402̄ w. m.	804̄ w. m.		
02(10) w. m.				

TABLE VI.

General planes.

113 w.m., m.	12̄1 s.	211 m.	22̄3 m.	311 w. m., m.	411 w. m., m.
114 w. m.	120 s.	212 w.	22̄4 w. m.	315 m.	412 m.
115 m. s., s.	12̄2 m. s.	213 m.	225̄ w.m.	317 w. m.	413 v. w.
116 w. m.	124̄ m.s.	215 w. m.	226̄ w.m.	318 w. m.	415 v. w.
117 m	125̄ w.	217 m. s.	227̄ w.m., m.	319 w.	416 v. w.
118 m.	126̄ w.m.	219 v. w.	228̄ m.s., m.	31̄3 m. s.	417 m.
11(10) v. w.	12̄9 w.	21̄1 m. s.	229̄ m.s.	31̄4 v. s.	41̄2 w.
11̄3 m.		21̄2 w.		31̄5 m.	41̄3 w.
11̄4 w. m.		21̄3 v. s.		31̄6 m. s.	41̄6 w.
11̄5 v s.		21̄5 w.		31̄7 m. s., s.•	41̄7 w. m., m.
11̄7 v s.		21̄6 m. s.		31̄9 w.	421 m.
11̄8 w. m.		21̄7 w. m., m.		322 w. m.	424 w. m.
11̄9 m. s., s.		21̄8 w. m.		324 m.	42̄1 v. w.
121 w.		21̄9 m s., m.		326 w.	
122 w. m., m.		221 w. m.		328 w.	
123 w.		222 w.		32̄2 w. m.	
124 w		226 w.m.		323 w.	
126 w.		227 w.		32̄4 w. m.	
		22̄1 w. m.		32̄6 w. m., m.	
		22̄2 m., m. s.		32̄7 m.	

TABLE VI (contd.):

General planes.

5̄11 w. m.	611 w.
512 m.	613 w.
513 w̄.	61̄1 w m.
517 w̄.	61̄3 w.
5̄11 w. m., m.	615 v. w.
51̄2 m. s.	61̄7 w.
513̄ w.	
51̄5 w.	
519 m. s.	
521 w.	
522 v. w.	
524̄ w. m.	

The lengths of the axes determined from the rotation photographs (Plate III, Fig. 1—3) about a, b and c axes are $a = 12·95$ Å; $b = 5·04$ Å; $c = 21·31$ Å.

These give the axial ratio $a : b : c = 2·569 : 1 : 4·229$ which is in good agreement with that mentioned above.

The list of reflecting planes observed in the crystal with their approximate relative intensities is given in Tables V and VI.

It will be seen from these that planes (hol) are halved when either h or l or (h+l) is odd and (olo) is also halved. This shows that the crystal belongs to the space group C_{2h}^5 which requires four asymmetric molecules in in the unit cell. The number of molecules in the unit cell calculated from its dimensions and the density of the crystals which was found to be $1·61$, is 8 (accurately $8·03$). This again leads to the conclusions that two molecules of p-nitrobenzoic acid associate together to form one asymmetric unit present in the unit cell.

The association of molecules in the unit cell observed in the case of m- and p-nitrobenzoic acids is not an improbability and has been observed in several cases by previous workers (*cf.* Caspari, *Phil. Mag.*, 1927, **4**, 1276 ; Prasad, D'Souza and Shanker, *J. Univ. Bombay*, 1936 ; Banerjee. *Proc. Ind. Sci. Cong.*, 1937).

PLATE III.

Rotation photographs of p-nitrobenzoic acid.

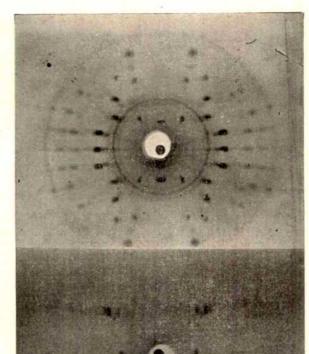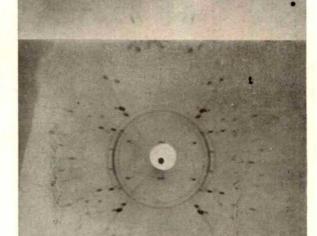FIG. 1.

a-axis
$D = 4·00$ cm.

FIG. 2

b-axis
$D = 4·00$ cm.

FIG. 3.

c-axis
$D = 4·00$ cm.

SYNTHETICAL EXPERIMENTS IN THE GROUP OF SYMPATHOMIMETICS. PART I. THE NAPHTHALENE SERIES.

BY S. RAJAGOPALAN.

A number of substituted β-naphthylethylamines possessing the requisite structure necessary for sympathomimetic activity has been synthesised.

Sympathomimetic amines have, in recent years, found extensive use in clinical practice. Though Madinaveitia (*Bull. Soc. chim.*, 1919, **25**, 5c1 ; *Anal. fis. quim.*, 1920, **18**, 66) has observed that the mere substitution of the naphthalene ring for the phenyl group in such bodies augments their physiological activity by over forty times, only a few sympathomimetics derived from naphthalene have been investigated. It was, therefore, considered interesting to study substituted β-naphthylethylamines and compare their physiological activity with the corresponding benzene analogues.

In the present communication the following compounds possessing the requisite structure for sympathomimetic activity have been prepared :

$R \cdot CH(OH) \cdot CH_2 \cdot NH_2, HCl.$

(I, R = α-or β-naphthyl-)

$R_1 \cdot CO \cdot CH_2 \cdot NC_5H_{10}, HCl$

(III, $R_1 = p$-methoxynaphthyl- or 5-acenaphthyl-)

$$\begin{array}{c} R \\ \diagdown \\ R \diagup \end{array} C(OH) \cdot CH_2 \cdot NH_2, HCl$$

(II, R = α-naphthyl-)

$R_2 \cdot CO \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 R_3$
HCl

(IV, $R_2 = p$-hydroxynaphthyl-;
$R_3 = 3 : 4$-dihydroxyphenyl-)

p-Hydroxy-ω-aminoacetonaphthone hydrochloride (Madinaveitia, *loc. cit.*) and β-naphthylethylamine (Meyer *et al.*, *Ber.*, 1922, **55**, 1885) have now been synthesised in good yields by easier methods.

Numerous attempts have been made to prepare p-hydroxynaphthyl-ethylamine. The experiments to condense either β-ethoxyethylamine or β-aminoethanol with α-naphthol under a variety of conditions have not been successful. In view of the fact that substituted glycyl chlorides are known to react readily with α-naphtholmethyl ether in presence of anhydrous aluminium chloride (Dey and Rajagopalan, *Proc. Nat. Inst. Science India*, 1940, **6**, 135) a detailed investigation has been made to bring about a Friedel-

Craft reaction between α-naphthol methyl ether and N-benzoyl-, naphthoyl-
or benzenesulphonyl-β-bromoethylamides. While in nitrobenzene solution
the naphthol ether is found to undergo the Scholl reaction (*Ber.*, 1922,
55, 109) giving 4:4'-dimethoxydinaphthyl, the reactants are recovered
unchanged when petroleum ether is used as diluent. Owing to the low
yields of the intermediates, the preparation of the desired amine from
p-ethoxybromonaphthalene, *via* the related ethyl bromide, had to be aban-
doned.

The synthesis of a 3:4-dihydroxynaphthylethylamine has been precluded
by low yields of 3:4-dimethoxy-*N*-benzoyl-ω-aminoacetonaphthone, obtained
by condensing hippuryl chloride with 1:2-dimethoxynaphthalene. The
attempt to bring about a Hoesch reaction between 1:2-dimethoxynaphthalene
and chloroacetonitrile, gives very poor yields. Morgan and Vining (*J. Chem.
Soc.*, 1921, **119**, 177) also experienced difficulty in substituting 1:2-dihydroxy-
naphthalene due to strong steric hindrance.

While experiments towards synthesis of diketones of the types
$(R \cdot CO \cdot CH_2)_2NH$ and $(RCO \cdot CH_2NH)_2CH_2$ $(R = C_{10}H_7)$ have been fruitless,
it has been possible to prepare compounds (II) and (IV).

The examination of the physiological activity of these products is in
progress.

EXPERIMENTAL.

β-Hydroxy-β-naphthyl-1-ethylamine Hydrochloride.—*N*-Acetyl-β-hy-
droxy-β-naphthyl-1-ethylamine (2.5 g.), prepared by the method of Pictet and
Manevitch (*Arch. Sci. Phys. Nat*, 1913, iv, **35**, 40), was hydrolysed by
refluxing with hydrochloric acid (1:3, 50 c.c.) for 2 hours. After filtering,
the clear liquid was evaporated to dryness at a moderate temperature. The
hydrochloride (1·8 g.) was crystallised from a mixture of alcohol and ether
in colourless needles, m.p. 156-57°. (Found : N, 6·5. $C_{12}H_{14}ONCl$ requires
N, 6·26 per cent). The *picrate* was yellow crystalline powder from water,
decomposing at 185°. (Found : N, 13·28. $C_{18}H_{16}O_8N_4$ requires N, 13·74
per cent).

β-Hydroxy-β-naphthyl-2-ethylamine hydrochloride was obtained by
similar hydrolysis of *N*-acetyl-β-hydroxy-β-naphthyl-2-ethylamine, synthe-
sised by Dey and Rajagopalan (*loc. cit.*) from β-acetonaphthone. It was
obtained as colourless plates from alcohol-ether, decomposing at 180-83°.
(Found : N, 6·40. $C_{12}H_{14}ONCl$ requires N, 6·26 per cent). The *picrate* was
obtained as a yellow powder from alcohol, decomposing at 191-92°.
(Found : N, 13·52 $C_{18}H_{16}O_8N_4$ requires N, 13·74 per cent).

4-Methoxy-ω-piperidinoacetonaphthone Hydrochloride.—A mixture of p-methoxy-ω-iodoacetonaphthone (5 g.), prepared according to Dey and Rajagopalan *(loc. cit.)* and piperidine (2·6 c.c.) in dry benzene (60 c.c.), was refluxed for 1 hour, cooled and poured into water. The benzene layer was washed thoroughly, dried and the hydrochloride isolated by passing in a stream of dry hydrogen chloride. It crystallised from alcohol-ether in colourless needles, decomposing at 233-34°. (Found : N, 4·27 ; Cl, 11·18. $C_{18}H_{22}O_2NCl$ requires N, 4·38 ; Cl, 11·11 per cent). The *picrate* was obtained as stout golden-yellow rods from acetic acid, decomposing at 150°. (Found : N, 11·20. $C_{24}H_{24}O_9N_4$ requires N, 11·32 per cent)   Attempt to prepare the corresponding 4-hydroxy compound by demethylation with hydrochloric acid in a sealed tube gave rise only to non-basic tarry material.

ω-Amino-5-acetoacenaphthone —ω-Iodacetoacenaphthone, prepared from known chloroketone (Meyer and Kaufmann, *Ber.*, 1920, 53, 295) and sodium iodide in acetone, crystallised as colourless plates from alcohol, m.p. 112-14°. (Found : I, 38·81. $C_{14}H_{11}OI$ requires I, 39·44 per cent). A mixture of equimolecular quantities of ω-iodo-acenaphthone and urotrophine in chloroform on standing overnight furnished quantitatively the addition compound, m.p. 160°. (Found : N, 11·42. $C_{20}H_{23}ON_4I$ requires N, 12·13 per cent). Hydrolysis of the addition compound with alocoholic hydrochloric acid (Mannich and Hahn, *Ber.*, 1911, 44, 1542) gave the unstable base hydrochloride, which was characterised as the *picrate* as yellow powder from alcohol, decomposing at 147-50° (Found : N, 12·60. $C_{20}H_{16}O_8N_4$ requires N, 12·73 per cent).

ω-Piperidino-5-acetoacenaphthone hydrochloride, obtained by interaction of ω-iodo-5 acetoacenaphthone and piperidine, separated as colourless needles from alcohol-ether, decomposing at 235 7°. (Found : N, 4·28 ; Cl, 10·22. $C_{19}H_{22}ONCl$ requires N, 4·44 ; Cl, 11·25 per cent). The *picrate* was obtained as yellow plates from acetic acid decomposing at 152°. (Found : N, 11·02. $C_{25}H_{24}O_8N_4$ requires N, 11·05 per cent).

4-Hydroxy-ω-aminoacetonaphthone Hydrochloride.—4-Methoxynaphthacylphthalimide (1·25 g.) (Dey and Rajagopalan, *loc. cit.*) was heated with concentrated hydrochloric acid (4 c.c.) in a sealed tube for 4 hours at 160-70°. The reaction product crystallised from alcohol-ether in colourless plates, m.p. 154-5°. The *picrate* melted at 186-87° (Dey and Rajagopalan, *loc. cit.*). Alternate methods were found to consist in similar hydrolysis of 4-methoxy-N-acetyl- or N-benzoyl-ω-aminoacetonaphthone (Dey and Rajagopalan, *loc. cit.*).

4-Methoxy-N-acetyl-β-hydroxy-β-naphthylethylamine, obtained by the reduction of 4-methoxy - N - acetyl - ω - aminoacetonaphthone with sodium

amalgam, separated from toluene in colourless, prismatic needles, m.p. 155-6°. (Found : C, 70·0 ; H, 6·54. $C_{15}H_{17}O_3N$ requires C, 69·5; H, 6·56 per cent). Attempts to hydrolyse the N acetyl or N-benzoyl derivative to p-hydroxy-β-hydroxy-β-naphthylethylamine were unsuccessful.

β-1-Naphthylethylamine Hydrochloride: (i) β-Naphthylethylphthalimide was obtained by refluxing an alcoholic solution of β-naphthylethyl bromide with potassium phthalimide at 100° for 8 hours as colourless, prismatic needles from alcohol, m.p. 143°. (Found: N, 4·56. $C_{20}H_{15}O_2N$ requires N, 4·65 per cent). (ii) Hydrolysis of the phthalimide derivative with concentrated hydrochloric acid in a sealed tube gave 60% yield of the hydrochloride, decomposing at 244-45°. (cf. Meyer et al., loc. cit.).

N-α-Naphthoyl-β-bromoethylamide, colourless plates from benzene-petroleum ether, m.p. 94°, (Found: N, 5·10. $C_{13}H_{12}ONBr$ requires N, 5·04 per cent) and N-benzenesulphonyl-β-bromoethylamide, m.p. 58°. (Found : N, 5·18. $C_8H_{10}O_2NBrS$ requires N, 5·30 per cent) were prepared by the action of the corresponding acid chlorides on β-bromo-ethylamine hydrobromide in the presence of sodium carbonate solution.

4 : 4'-Dimethoxydinaphthyl.—To a well-cooled solution of anhydrous aluminium chloride (45 g.) in dry nitrobenzene (7·5 c.c.), were successively added α-naphthol methyl ether (5 g.) and N-benzoyl-β-bromoethylamide (7 g.) with constant agitation. After standing overnight and decomposition with ice and dilute hydrochloric acid the dimethoxydinaphthyl (3·6 g.) was filtered, washed with water, dilute alkali, acetic acid and crystallised from nitrobenzene in colourless rectangular plates, m.p. 254-55°. The same product was obtained even in the absence of N-benzoyl-β-bromo-ethylamide. The mixed m.p. of this specimen with an authentic sample of 4 : 4'-dimethoxydinaphthyl (Östermeyer and Renhek, *Ber.,* 1889, 17, 2454) was not depressed.

Experiments towards the Synthesis of p-Hydroxynaphthylethylamine: (i) 4-Ethoxy-β-naphthylethyl alcohol was obtained by the action of ethylene oxide (18·5 c.c.) in ether on a Grignard reagent from p-ethoxy-bromonaphthalene (70 g.), magnesium (7 g.) and a mixture of dry ether (400 c.c.) and dry benzene (100 c.c.) and purified by distillation as colourless oil (22 g.), b.p. 178-86°/2-3 mm. The *picrate* was obtained as brilliant red needles, m.p. 104-5°. (Found: N, 9·14. $C_{20}H_{19}O_9N_3$ requires N, 9·44 per cent). (ii) 4-Ethoxynaphthylethyl bromide, prepared by the action of phosphorus tribromide on the alcohol at room temperature, was converted into 4-ethoxy-β-naphthylethyl phthalimide in poor yields in the usual way and obtained as colourless needles from alcohol, m.p. 175°. (Found :

N, 4·07. $C_{22}H_{19}O_3N$ requires N, 4·06 per cent). (*iii*) Urotropine reacted with the ethyl bromide to give also a poor yield of the addition compound as colourless, amorphous powder, decomposing at 189°. (Found : N 12·74 $C_{20}H_{27}ON_4Br$ requires N, 13·37 per cent).

3 : 4-*Dimethoxy*-N-*benzoyl*-ω *aminoacetonaphthone.*—To a mixture of 1 : 2-dimethoxynaphthalene (6·3 g.) and hippuryl chloride (8 g.) in carbon disulphide (40 c.c.) was gradually added finely powdered anhydrous aluminium chloride (6 g.) The mixture, after heating on the water-bath for 2 hours, standing overnight and working up in the usual way, yielded the ketone (0·8 g.) in colourless, hair-like needles from acetone, m p. 261-2°. (Found : N, 4·10 $C_{21}H_{23}O_4N$ requires N, 4·08 per cent).

N- p - *Hydroxynaphthacyl*-3 : 4-*dihydroxyphenylethylamine hydrochloride.*—N-*Benzenesulphonylhomoveratrylamide* separated from alcohol as colourless, prismatic needles, m. p. 89°. (Found : N, 4·79. $C_{16}H_{19}O_2NS$ requires N, 4 81 per cent). To the sodium salt of the above amide in alcohol (50 c.c.) 4-methoxy-ω-iodoacetonaphthone (4 g.) was added and the mixture refluxed on the water-bath for 4 hours. The crude 4-methoxynaphthacyl derivative (4 g.) purified through an ethereal solution, was heated in a sealed tube with concentrated hydrochloric acid (15 c.c.) for 5 hours at 170-80°. The aqueous solution of the hydrochloride (Norit) was evaporated in vacuo over sulphuric acid. It separated as colourless needles (0·8 g.) from alcohol-ether, decomposing at over 180°. (Found : N, 3·55. $C_{20}H_{20}O_4NCl$ requires N, 3·75 per cent). The *picrate* was obtained as orange-red needles from water, decomposing at 189-91°. (Found : N, 9·82 $C_{26}H_{22}O_{11}N_4$ requires N, 9·89 per cent).

N-*Benzenesulphonyl*-ω-*amino*-α-*acetonaphthone* was obtained as colourless needles from acetic acid, m.p. 121°. (Found : N, 4·28. $C_{18}H_{15}O_3NS$ requires N, 4·31 per cent). N-*Benzenesulphonyl*-ω-*amino*-β-*acetonaphthone,* obtained as colourless, prismatic needles from acetic acid, melted at 165°. (Found : N, 4·24. $C_{18}H_{15}O_3NS$ requires N, 4·31 per cent).

4-*Methoxy*-ω-*aminoacetonaphthone Hydrochloride.*—Hydrolysis of the N-acetyl derivative with dilute hydrochloric acid gave in quantity the hydrochloride in colourless needles from water decomposing at 204°. (Found : N, 3·15. $C_{13}H_{14}O_2NCl$ requires N, 3·41 per cent). The *picrate,* golden yellow plates from alcohol, decomposes at 191°. (Found : N, 12.76. $C_{19}H_{16}O_9N_4$ requires N, 12·82 per cent). N-*Benzenesulphonyl derivative,* obtained as colourless needles from acetic acid, melts at 147°. (Found : N, 3·89. $C_{19}H_{17}O_4NS$ requires N, 3·94 per cent).

N-β-1-*Naphthylethyl-benzenesulphonylhomoveratryl* amide, obtained by treating β-1-naphthylethyl bromide with the sodium salt of benzene-

sulphonylhomoveratryl amide in alcohol solution, separated as colourless, rectangular plates, m.p. 82-83°. (Found: N, 2·96. $C_{28}H_{29}O_4NS$ requires N, 2·95 per cent).

$\beta:\beta$-1 : 1'-*Dinaphthyl-β-hydroxyethylamine Hydrochloride.*—A Grignard reagent from β-bromonaphthalene (91 g.), magnesium (8·5 g.) and ether (35 c.c.) was treated with ω-amino-a-acetonaphthone hydrochloride (12·8 g.) in the course of 10 minutes, the mixture gently boiled for 2 hours on the water-bath after standing at room temperature for 1 hour and then decomposed with cold dilute hydrochloric acid. The hydrochloride (9.5 g) was filtered and washed with ether. It was obtained as colourless prismatic needles from alcohol, decomposing at 260°. (Found: N, 4·02 ; Cl, 8·99. $C_{22}H_{20}ONCl$ requires N, 3·99 ; Cl, 10·13 per cent). The *piciate*, shining yellow needles or plates from acetic acid, decomposes at 168°. (Found: N, 10·69. $C_{28}H_{22}O_8N_4$ requires N, 10·31 per cent).

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SYNTHESIS OF 3-(p-HYDROXYPHENYL)-CYCLOHEXANONE

BY D. K. BANERJEE.

A synthesis of 3-(p-hydroxyphenyl)-cyclohexanone, which consists of a hydrogenated diphenyl nucleus, has been described. The above ketone was expected to be oestrogenically active, but experimental results according to Allen-Doisy test were found to be negative up to the maximum dose of 8 mg.

In course of an investigation on the possible oestrus-producing activity of synthetic substances (Cook *et al.*, *Proc. Roy. Soc.*, 1934 **114B**, 272, 286), made the important discovery that the oestrogenic activity is extraordinarily unspecific and that the oestrus change can be induced by numerous substances bearing little resemblance to the hormone itself. In their earlier investigations, one of the simplest substances to be found oestrogenically active was 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (*Naturwiss.*, 1933, **21**, 222 ; *Nature*, 1933, **131**, 56, 205) and the first active compound, in which the phenanthrene nucleus was absent was found to be 1: 2-dihydroxy-1 : 2-di-α-naphthylacenaphthene (*Nature*, 1936, **137**, 996) Simpler molecules were then studied and substances such as 4:4'-dihydroxy diphenyl, *p*-hydroxypropenylbenzene (Dodds and Lawson, *Nature*, 1937 **139**, 627, 1068 *et seq.*) were also found to possess oestrogenic activity. From consideration of the above it seemed to be of interest to investigate the physiological property of the ketone (I).

(I)

The present communication deals with a method for the synthesis of the above ketone. Ethyl γ-anisoylbutyrate (II) has been treated with zinc

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and ethyl bromoacetate in benzene solution to yield the lactone of r-carbethoxy-2- (p-methoxyphenyl) - 2 - hydroxypentane-5-carboxylic acid (III). β-(p-Methoxyphenyl)-pimelic acid (IV) is obtained by reducing the above lactone with zinc dust and 10% sodium hydroxide solution. Both the ethyl and methyl esters of the dibasic acid (IV) are cyclised by means of sodium in benzene solution. The resulting crude β-ketonic ester, which,, however, could not be distilled without decomposition in vacuum, yields on hydrolysis with 20% sulphuric acid 3-(p-methoxyphenyl)-cyclo-hexanone (V). 3-(p-Hydroxyphenyl)-cyclohexanone (I) is obtained by demethylation of the above methoxyketone with hydrobromic acid.

(II)   (III)

(R' = H,Me,Et)

(IV) → (V) → (I)

$$\left[\quad R = \quad MeO\text{—} \quad \text{in the above formulæ} \quad \right]$$

The above compound is found in the Allen-Doisy test to be inactive up to the dose of 8 mg., when injected into castrated mice. In this connection, however, the work of Butenandt and Schramm (*Ber.*, 1935, 68, 2083, 2303), who prepared the 7-hydroxy derivative of 1-keto-1:2 : 3: 4-tetrahydrophenanthrene, may be mentioned. Their ketone is also found inactive in the Allen-Doisy test up to 9 mg.

EXPERIMENTAL.

Ethyl γ-Anisoylbutyrate (II).—γ-Anisoylbutyric acid was prepared by modifying the method of Plant and Tomlinson (*J. Chem. Soc.*, 1935, 856) To an ice-cold solution of finely powdered dry aluminium chloride (70 g.) in dry nitrobenzene (250 c.c.), was added dropwise with constant shaking a mixture of glutaric anhydride (30 g.) and anisole (30 g.). The thick red coloured mass was allowed to stand at the room temperature for 48 hours, and then decomposed with ice and hydrochloric acid. Nitrobenzene was removed by steam distillation, when γ-anisoylglutaric acid separated in fine crystals on cooling and was filtered off. The crude product was purified by dissolving in sodium bicarbonate solution and acidification. The acid (50 g.) was refluxed with a mixture of ethyl alcohol (200 c.c.) and sulphuric acid ($d \cdot 1 \cdot 84$, 12 c.c.) for 6 hours on a boiling water-bath. The ester was isolated in the usual manner, when it boiled at 193-95°/5-6 mm., as a colourless liquid, which quickly solidified and on crystallisation from ethyl alcohol separated in white needles, m.p. 59-60°. (Found : C, 67.1 ; H, 7·08. $C_{14}H_{18}O_4$ requires C, 67·2 ; H, 7·2 per cent). The *semicarbazone* on crystallisation from ethyl alcohol melted at 120-21°. (Found : N, 13·66. $C_{15}H_{21}O_4N_3$ requires N, 13·68 per cent).

Lactone of 1-*Carbethoxy-2-(p-methoxyphenyl)-2-hydroxypentane-5-carboxylic Acid* (III)— The keto-ester (II) (42 g.), ethyl bromoacetate (42 g., 1·5 mols) and zinc wool (21 g.) in dry benzene (120 c.c.) were taken in a flask provided with an efficient reflux condenser and heated on a water-bath, with the addition of a crystal of iodine. The reaction started after about ½ hour and grew vigorous, when it was necessary to remove the flask from the water-bath. After the vigorous reaction had subsided, the flask was replaced on the water-bath and the heating was continued for further 2 hours. The reaction mixture was cooled and decomposed with ice and dilute sulphuric acid. The benzene layer was washed with water and then extracted with 10% sodium carbonate solution, in which the δ-lactone dissolved freely in the cold. The alkaline solution was acidified and extracted with ether.

The extract was washed with water and .dried. Ether was removed and the lactone was distilled at 229-30°/4 mm., yield 35 g. (Found : C, 65·61 ; H, 7·15. $C_{16}H_{20}O_5$ requires C, 65·75 ; H, 6·84 per cent).

β-(p-Methoxyphenyl)-pimelic Acid (IV).—A solution of the lactone (20 g.) in 10% sodium hydroxide solution (500 c.c.) was placed in a two-necked flask, provided with a reflux condenser and a mercury-sealed stirring arrangement. Zinc dust (75 g.) was added to the solution and the contents were heated to boiling and mechanically stirred for 18 hours. The zinc was filtered off and an excess of concentrated hydrochloric acid added to the filtrate. The white precipitate, thus obtained, was filtered off and redissolved in 10% sodium carbonate solution. The solution was filtered off from undissolved impurities and acidified. The dibasic acid, so obtained, was collected, washed well with water, dried and crystallised from dilute ethyl alcohol, m.p. 154-56°. (Found : C, 63·22 ; H, 6·78. $C_{14}H_{18}O_5$ requires C, 63·15 ; H, 6·76 per cent). For the preparation of diethyl and dimethyl esters of the acid (IV), the following method was used. The crude acid, obtained by acidification of the filtered alkaline solution, was extracted with benzene, and the benzene layer well dried over sodium sulphate. The residue, left after removal of benzene, was refluxed with ethyl or methyl alcohol (100 c.c.) and sulphuric acid (d 1·84, 10 c.c.) for 12 hours. On working up in the usual manner, the diethyl ester was collected at 195-205°/4-5 mm. and redistilled at 199-201°/4-5 mm. (Found : C, 67·2 ; H, 7·83. $C_{18}H_{26}O_5$ requires C, 67·08 ; H, 8·07 per cent). The dimethyl ester was also collected at 187-95°/4-5 mm., and redistilled at 190-93°/4-5 mm. (Found : C, 65·2 ; H, 7·37. $C_{16}H_{22}O_5$ requires C, 65·3 ; H, 7·48 per cent).

3-(p-Methoxyphenyl)-cyclohexanone (V).— Dimethyl β-(p-Methoxyphenyl)- pimelate (7·3 g.) in dry benzene (25 c.c.) was refluxed with sodium dust (1·1 g.) until all the sodium went into solution (ca. 2 hours). The solution was cooled and treated with ice and dilute sulphuric acid. The benzene layer was separated and washed successively with dilute sodium bicarbonate solution and water and dried. The benzene was removed and on attempting to distil the oil, it was found to decompose. The crude oil, which gave a reddish violet colouration with alcoholic ferric chloride, was refluxed with an excess of 20% sulphuric acid for 12 hours. The resulting oil was extracted with ether and the ethereal layer washed with water and dilute sodium bicarbonate solution, dried and the ether removed. The residual brown oil on distillation in vacuum solidified. It was crystallised from benzene-petroleum ether (40-60°), m.p. 83°. (Found : C, 76·28 ; H, 7·76. $C_{13}H_{16}O_2$ requires C, 76·47 ; H, 7·84 per cent).

The *semicarbazone* of the above ketone, on crystallisation from ethyl alcohol, melted at 217-19°. (Found : N, 16·02. $C_{14}H_{19}O_2N_3$ requires N. 16·09 per cent).

3-(*p-Hydroxyphenyl*)-cyclo*hexanone* (I).—The methoxyketone (V) (1·5 g.) was heated with acetic acid (23 c.c.) and hydrobromic acid (23 c. c., d 1·49) at 110° for 3-4 hours. The cooled solution was diluted with water and extracted with ether. The ethereal layer was washed with water and the hydroxy-ketone was extracted by shaking it with 10% sodium hydroxide-solution. After acidifying the alkaline solution, the hydroxy-compound was taken up in ether, the ethereal layer washed and dried and the ether removed. The residue, on distillation in vacuum, solidified to a yellow crystalline mass, m.p. 155-58°. On recrystallisation from benzene it melted at 159-61°. (Found : C, 75·69 ; H, 7·28. $C_{12}H_{14}O_2$ requires C, 75·78 ; H, 7·36 per cent).

My best thanks are due to Prof. P. C. Mitter for his advice and the keen interest taken during the progress of the work. My thanks are also due to Mr. S. K. Saha for carrying out the micro-analysis of some of the compounds and to Messrs I. G. Farbenindustrie, A.-G. for carrying out biological assay of the hydroxyketone (I) in June 1937

THE AMYLASE ACTIVITY OF SWEET CASSAVA (MANIHOT PALMATA).

By K. S. Murty.

In view of the lack of knowledge regarding the amylolytic enzymes of tubers, the amylase activity of sweet cassava has been studied. The results obtained will be of considerable interest in the manufacture of starch from cassava.

In view of our meagre knowledge of the amylase activity of tubers it was thought desirable to investigate the amylase from cassava (*Manihot Palmata*). Cassava is widely cultivated in the tropics. Its mineral requirements being very low, it is particularly well adopted for cultivation on poor sandy soils. The yield on a well irrigated land may amount to 15—16 tons per acre. According to the analysis of Leuscher (*Offentl. Chem.* 1902, 8, 10) the fresh tuber contains water (70·25%), protein (1·12%), fat (0·41%), starch (21·44%), sugar (5·13%), crude fibre (1·11%), and ash (0·54%).

There are two varieties of cassava tubers, the sweet and the bitter. Francis (*Analyst*, 1878, 2, 4) found 0·0168% of hydrocyanic acid in the sweet cassava (*Manihot palmata*) root and 0·0275% in the bitter cassava (*Manihot utilissima*) root. Cellens (*Bull. Dept. Agric., Trinidad and Tobago*, 1915, 14, 54) found 0·0048% of hydrocyanic acid in the roots of the sweet variety and 0·0053% in the roots of the bitter variety. The leaves and the stems also contain hydrocyanic acid. The leaves of the sweet and the bitter varieties contain 0·0162% and 0·041% of hydrocyanic acid respectively and the pealings of the stems 0·043% and 0·113% respectively.

It will be seen from the above analysis that cassava contains a very high percentage of starch and very low percentage of mineral matter. It should, therefore, prove particularly valuable for the manufacture of starch.

EXPERIMENTAL.

Fresh tubers of the sweet variety were obtained direct from the fields. The thick outer skin was removed and the skinned tuber was chopped into very thin slices, which were dried in the sun, powdered and sieved. The powder could be well preserved in bottles, for considerable length of time without any deterioration.

Preparation of the Enzyme-Extract.—60 G. of the powder were ground into a thin paste with about four times the quantity (250 c.c.) of water. This was transferred into an Erlenmeyer flask and toluene (2-3 c.c.) was added to avoid bacterial action thereby preventing a fall in the activity of the enzyme. This was kept for 24 hours and the clear liquid above was decanted into a separate flask. This was used for subsequent work.

Method of Procedure.—Pure soluble starch (Schering) was used as the substrate. The hydrogen ion concentration of the reaction medium was adjusted by the addition of Sörensen's phosphate buffers of p_H values 5·6 to 8·0 and Walpole's acetate buffers for p_H values 3·0 to 5·0. Enzyme extract was prepared (as described above) afresh for each experiment.

The experiments were carried out in Erlenmeyer flasks. Controls were set up for each experiment with starch alone, without the addition of the enzyme. After hydrolysis, the maltose formed was estimated by the iodometric method of Willstätter and Schüdel (*Ber.*, 1918, **41**, 780).

Influence of Temperature on the Enyme Activity.—The activity of the enzyme was studied at temperatures varying from 30°-70° at intervals of 5°. The p_H of the buffer used was 6·8. Each experiment consisted of a set of two flasks (referred to in the table as I and II).

I. Enzyme and starch.		II. Starch alone.	
2·5% Starch soln.	9 c.c.	2·5% Starch soln.	9 c.c.
Buffer soln.	5 c.c.	Buffer soln.	5 c.c.
Enzyme extract	1 c.c.	Water	1 c.c.

TABLE I.

Temp. ($\pm$0·1°).	Maltose formed in 30 minutes.		Temp. ($\pm$0·1°).	Maltose formed in 30 minutes	
30°	24·0 mg.	18·0 mg.	50°	24·9 mg.	21·0 mg.
35°	24·0	18·8	55°	27·6	21·2
40°	24·9	18·8	60°	26·7	21·2
45°	24·9	20·6	70°	26·6	21·2

From the above results it is evident that the optimum temperature for the enzyme activity is about 55°.

Influence of p_H on the Enzyme Activity.—Hydrogen ion concentrations varying from p_H 3 to 8 were studied at intervals of about 0·5. The temperature was maintained throughout the course of the experiment at

30°. Controls were set up as in the previous experiment and the results obtained are given in mg. of maltose formed in 30 minutes.

TABLE II.

p_H	I.	II.	p_H	I.	II.
3.0	24·8 mg.	21·2 mg.	6·2	25·8 mg.	18·0 mg.
3·8	24·9	21·2	6-5	27·5	18·8
4·4	24·9	21·2	6·7	25·8	18·8
5·0	25.7	18·0	7·0	25·7	18·9
5·6	25·8	17·1	7·4	24·0	20·6
5·9	25·8	17·2	8·0	24·0	23·2

It is evident from the above results that the optimum p_H for the enzyme activity is about 6·5.

The author desires to express his indebtedness to Dr. G. Gopala Rao of the University College, Waltair, for suggesting the problem. He also thanks Dr. K. V. Giri of the Andhra University, Waltair, and Mr. P. V. Krishna Murty of the Andhra Medical College, Vizagapatam, for their kind encouragement.

THE EFFECT OF INORGANIC COLLOIDS ON THE ELECTRO-DEPOSITION OF NICKEL ON COPPER.

By V. S. Puri and G. C. Juneja.

A quantitative study of the effect of selenium, aluminium hydroxide, ferric hydroxide, iodine and sulphur sols on the deposition of nickel on copper has been made The first three sols considerably increase the hardness and lustre of the deposit, iodine much less and sulphur has a negative effect altogether. Explanations have been attempted for their interesting behaviour.

Puri and Bhatia (*J. Indian Chem. Soc.*, 1937, **16**, 71) studied the effect of inorganic colloids on the electrodeposition of nickel on copper. They found the presence of silver and Prussian blue hydrosols in the bath solution to increase the lustre of the plates. Arsenious sulphide was found to have an adverse effect in so far as it gave dull looking, rough and spongy deposits. Pring and Taiton (*J. Chem. Soc.*, 1914, **105**, 710), Wernick (*Trans. Faraday Soc.*, 1920, **24**, 361) and Merce (*Z. Elektrochem.*, 1913, **19**, 31) noticed similar effects in the case of organic colloids like glue, gum, gelatin, egg-albumin, etc.

The present work deals with a quantitative study of the effect of selenium, sulphur, iodine, ferric hydroxide and aluminium hydroxide sols on the deposition of nickel on copper. Explanations have been attempted for their interesting behaviour.

EXPERIMENTAL.

The bath employed in the experiments was the same as used by Puri and Bhatia (*loc. cit.*) and the plates were subjected to a preliminary treatment in the same manner with the difference that a mixture of sulphuric and nitric acids was used in the final cleaning in order to expose the crystal structure and ensure a good deposit.

The sols were rendered free of electrolytes by electrodialysis. The dialyser was prepared in the following manner.

A wide mouthed glass cylinder was filled with collodion solution which was then poured out. The cylinder was rotated horizontally till the collodion remaining on the walls of the cylinder dried up. More collodion solution was poured in. A second layer was allowed to form as before. Collodion formed a layer on the walls of the cylinder from which

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it was carefully withdrawn. It was washed with distilled water. The sac thus obtained was partially filled with the colloid and put into another sac of linen of the same size. This was lowered in water containing the positive and negative electrodes. The driving force of the external voltage causes the removal of the ions of the electrolyte.

Selenium Sol.—Seienium dioxide (1 g.) was dissolved in 500 c.c. of water and 100 c.c. of 1% gelatin added to the warm solution. To this 600 c.c. of hydrazine hydrate were added drop by drop. It was kept a little below the boiling point for 15 minutes. A pink sol was formed which was found to be negatively charged.

Table I shows the effect of the sol on the electrodeposition of nickel. There is a slight increase in the weight of the metal deposited on account of a fall in the resistance of the cell. The deposit is coherent, fine grained and hard.

Addition of 5 c.c. of the sol (0·00093 g.) resulted in the reduction of the number of abrasion marks. The size of the grain is also much reduced.

Addition of 10 c.c. (0·00186 g.) of the sol increases the thickness of the deposit sufficient to cover the defects so as to cause it to take high polish. The deposit was very hard.
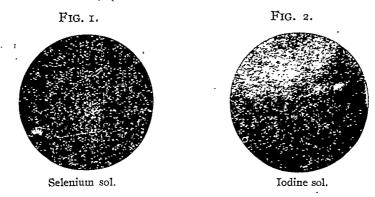
On the addition of 15 c.c. of the sol (0·00279 g.) the deposit ceases to be coherent as the crystal size increases. This confirms the view that there is an upper limit of the concentration beyond which the deposits obtained grow dull and spongy.

Sulphur Sol.—Sulphur dioxide was passed for 10 minutes into a saturated solution of hydrogen sulphide in water. The opaque liquid was boiled to remove sulphur dioxide. Sodium chloride was added to it and the coagulated particles were centrifuged The supernatant liquid was removed and the solid repeptised in water and dialysed. There was a negative charge on the sol.

Experiments showed that there is a wide discrepancy between the theoretical and the experimental values for the metal deposited. It seems there is a large increase in the resistance of the cell. Further the anode becomes black and spongy. There was no appreciable difference with 5 c.c. and 15 c.c. of the colloid.

Iodine Sol.—Iodine crystals were added cautiously to a 2% solution of sodium hydroxide until the straw yellow liquid just began to turn red. The unreacted iodine was removed Gum arabic (2 g.) was added at 0° and the mixture acidified with concentrated HCl. The colloidal iodine thus obtained was dialysed. The solution was negatively charged.

Our experiments showed that quantitatively there is no appreciable decrease in current density but with o˙0059 g. of the sol (Fig. 1) there is an effect on the crystal size and all the inherent defects of the plate disappear. If the quantity of the colloid is increased to o˙0118, the size of crystal increases and the deposit peels off easily.

FIG. 1.

FIG. 2.

Selenium sol.

Iodine sol.

Aluminium Hydroxide Sol.—A dilute solution of aluminium acetate (1% solution diluted twenty times) was warmed on a water-bath until the odour of acetic acid disappeared. The sol which resulted was very clear. It was carefully electrodialysed. It was positively charged. ·

Like selenium there is an increase in the weight of the metal deposited. Addition of o˙001144 g. and o˙00572 g. sol respectively makes the deposit hard, bright, coherent and abrasion marks of the original plate disappear.

Ferric Hydroxide Sol.—Ammonium hydroxide added drop by drop to ferric chloride solution (5 c.c. saturated ferric chloride solution in 100 c.c. water) till the supernatant liquid acquired a red tinge. The precipitate was repeatedly washed and then transferred to an Erlenmeyer flask. About 40 c.c. of water were then added and the mixture shaken. 5 c.c. of this liquid were poured into 100 c.c. of water along with a few drops of $N/10$ HCl. On standing an intensely red solution was obtained. It was electrodialysed and its charge was found to be positive.

Ferric hydroxide resembles selenium and aluminium hydroxide in its effects. The deposit becomes hard, close-grained and shining. The effect of addition of o˙00862 g. and o˙1724 g. of the colloid has been studied. Small crystals became visible and brightness diminished if the quantity of the sol is allowed to reach o˙02586 g.

It will be seen that in all the above cases small quantities of protective agents are employed to stabilize the colloids. These protective agents like

gum arabic, gelatin, tannin, etc., will have specific effects of their own. These effects, however, were not found to be comparable to those obtained above when these hydrophilic colloids alone were used. Microphotographs taken show that these agents are not so very active in the concentrations employed. Further, the effects obtained are those from colloidal suspensions and not from the sols in the general sense of the word. As the bath is highly electrolytic in nature, formation of such a suspension is inevitable but it has been observed that this suspension takes days to settle and if stirring is constantly done, it sets hardly at all. That the colloids have a marked effect on the amount and the nature of the deposit appears to be beyond any doubt. The results are shown below.

TABLE I.

Effect of sols on the electrodeposition of nickel on copper.

Colloid.	Ni deposited. Actual.	Ni deposited. Theoretical.	Increase or decrease in C.D.	Amount of colloid per litre of bath soln.	Appearance of deposit.
Selenium	0·1246g.	0·1245g.	—	0·00 g.	Rough shining hard deposit; variation in size of crystals.
	0·1177	0·1136	Incıease	0·0093	Closed and fine grained hard shining deposit; abrasion marks completely absent.
	0·1162	0·1134	Increase	0·00186	Do.
	0·1139	0·1102	Increase	0·00279	Bright deposit.
Sulphur	0·1734	0·1833	—	0·00	Deposit shining; abrasion marks quite visible.
	0·1149	0·1191	Decrease	0·002208	Velvety deposit of bluish black colour but shining deposit on the side not facing the anode.
	0·1187	0·1229	Decrease	0·004416	Do.
	0·1189	0·1232	Decrease	0·006624	Do.
Iodine	0·1230	0·1232	—	0·00	Hard, lustrous deposit
	0·1175	0·1150	Decrease	0·0059	Shining and very hard deposit.

TABLE I (contd.).

Colloid.	Ni deposited		Increase or decrease in C. D.	Amount of colloid per litre of bath soln.	Appearance of deposit.
	Actual.	Theoretical.			
	0˙1122 g.	0˙1190 g.	Decrease	0˙0118 g.	Large flat crystals of varying size.
	0˙0916	0 1187	Decrease	0˙0177	Voluminous non-adherent crystals.
Al (OH)₃	0˙1141	0˙1150	—	0˙00	...
	0˙1157	0˙1127	Increase	0˙001144	Not very hard; non-coherent, bright deposit.
	0˙1162	0˙1130	Increase	0˙00333	Very hard; all the abrasion marks absent, fine grained.
	0˙1167	0˙1130	Increase	0˙00572	Bright deposit
Fe (OH)₃	0˙1246	0˙1240	—	0˙00	...
	0 1178	0˙1143	Increase	0˙00826	Close grained, hard shining deposit.
	0˙1151	0˙1126	Increase	0˙01724	Fine grained, very hard and bright deposit.
	0˙1124	0˙1100	Increase	0˙02568	Deposit hard but not bright.

A NEW PROCESS FOR QUANTITATIVE ESTIMATION OF ANTIMONY AND ITS SEPARATION FROM TIN AND LEAD BY MEANS OF ALKALI SULPHOCYANIDES.

By H. N. Ray.

Antimony reacts with the alkali sulphocyanides in a moderately strong and boiling hydrochloric acid solution with the formation of antimony trisulphide. Tin and lead, if present, remain in solution. Nitric acid and nitrates must be absent and sulphuric acid gives high result even in the absence of lead due to separation of sulphur.

If to a cold hydrochloric acid solution of antimony, alkali sulphocyanides are added, the solution remains clear, no precipitate comes down. But if the solution is made to boil, a turbidity appears which gradually passes from orange-red to scarlet-red precipitate of the antimony compound. The reaction possibly occurs according to the following equations :—

$$KCNS + 2HCl + H_2O = KCl + NH_4Cl + COS$$
$$3COS + 2SbCl_3 = Sb_2S_3 + 3COCl_2$$

Evolution of H_2S gas during the reaction indicates a partial decomposition of the sulphide by the hydrochloric acid present. Hence the solution should be diluted for complete precipitation

Procedure.—Samples containing about 0·1 g. of antimony was weighed out in a 600 c.c. beaker and sufficient nitric acid (d 1·2) added to decompose the substance completely, followed by a few c.c. of HCl to dissolve the oxides formed. The solution was brought to a syrupy consistency by evaporating on a water-bath. HCl (20 c.c.) was again added and the solution evaporated to a small bulk. This process is repeated until the whole of HNO_3 was completely removed. The solution was made up to 125 to 150 c.c. containing 20 to 25 c.c. free hydrochloric acid. It was allowed to boil freely on the hot plate. A saturated solution of ammonium thiocyanate (25-30 c.c.) was then added to this boiling solution. A pink coloration appeared for a moment and red precipitate of Sb_2S_3 separated out. Ater a minute it was removed from the hot plate and allowed to settle for five minutes. The volume was then diluted upto 300 c.c. for complete precipitation of the sulphide. The precipitate was then quickly filtered through a weighed Gooch crucible, washed first with hydrogen sulphide water, then with

hot water to remove the chloride and sulphocyanide. Carbon disulphide washing followed next and it removed any free sulphur (if present) at this stage. Lastly, the precipitate was washed with alcohol and heated for two hours in a drying oven at 200° to 300°.

Fairly good results are obtained (when too much of tin or lead is present) by reprecipitating the sulphide with thiocyanate from acid (HCl) solution as described above. The weight of the precipitate multiplied by 71·42 gives the percentage of antimony.

Weight taken.	Sb₂S₃		Weight taken.	Sb₂S₃	
	Found	Calc		Found.	Calc.
Tartar emetic (0·4158 g.) + tin (0·5010 g.) + lead (0·20 g.)	0 2100 g.	0·2104 g.	Tartar emetic (0·4108 g.) + tin (0·1210 g.) + Pb-(NO₃)₂ (0·1010 g.)	0·1511 g.	0·1524 g.
Tartar emetic (0·4003 g.) + tin (0·4120) + lead (0·202 g)	0·2019	0·2025	Tartar emetic (0·3606 g) + tin (0·2008 g.) + Pb(NO₃)₂ (0 0998 g.)	0·1329	0·1340
Tartar emetic (0·3234 g.) + tin (0·10 g) + Pb·NO₃)₂ (0·015 g.)	0·1190	0·1202	Tartar emetic (0·1020 g.) + tin (0·1985 g.) + Pb-(NO₃)₂ (0·2088 g.)	0·0369	0.0379
Tartar emetic (0·1520 g.) + tin (0·0980 g.) + Pb(NO₃)₂ (0·2108 g.)	0·0538	0·0602			

It is better to keep tin in the higher state of oxidation, *i.e.*, in the stannic form before the sulphocyanides are added. Stannous tin has a tendency to fall down with antimony as sulphide. The behaviour of lead is somewhat different in this case. Lead remains in solution under the conditions of the experiment and is not precipitated either as chloride or sulphide.

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MERCURY DIALLYL AND ALLYL MERCURIC HALIDES.

BY K. V. VIJAYARAGHAVAN.

Mercury diallyl is formed as a colourless liquid on reducing allyl mercuric iodide with an aqueous solution of sodium stannite The compound is somewhat unstable at ordinary temperatures slowly depositing mercury and evolving diallyl. By treatment with bromi nein ether solution allyl mercuric bromide (m p. 124-125°) is obtained. By the action of 4% hydrochloric acid on mercury diallyl, allyl mercuric chloride (m.p. 102-103°) has been prepared.

Zinin (*Annalen*, 1855, **96**, 363) prepared allyl mercuric iodide by shaking together mercury and allyl iodide in alcohol with a trace of iodine. Recently Austin (*J. Amer. Chem. Soc.*, 1931, **58**, 3514) prepared lead triphenylallyl.

Several workers have attempted to prepare mercury diallyl from allyl mercuric iodide without success. Zinin states that C_3H_5HgI heated just above its melting point (134-35°) decomposes giving a gaseous product, (which he did not identify) leaving behind a carbonaceous residue. The preparation of mercury diallyl was, therefore, first attempted by the action of heat on C_3H_5HgI.

EXPERIMENTAL.

Purified allyl mercuric iodide (60 g.) from acetone was placed in an all glass distillation apparatus. After displacing the air by dry hydrogen and evacuating to about 1 mm., the substance was slowly heated in a paraffin oil-bath. Decomposition occurred at about 120°. The distillate (5-6 c.c.) consisted of a mixture of allyl iodide and diallyl. The residue consisted of mercurous iodide and free mercury only. The reactions are probably represented by the following equations :

$$C_3H_5HgI \longrightarrow C_3H_5I + Hg.$$
$$2 C_3H_5HgI \longrightarrow C_6H_{10} + Hg + HgI_2$$
$$HgI_2 + Hg \longrightarrow Hg_2I_2.$$

Allyl mercuric iodide was heated with an excess of potassium iodide in an all glass apparatus at about 1 mm. pressure, the residual gas being hydrogen, as before. Decomposition occurred at about 115°. The distillate was found to be again allyl iodide and diallyl, and the residue contained K_2HgI_4 and free mercury.

The above results suggest that mercury diallyl may be formed as an intermediate product but it decomposes at the temperature of the reaction.

The formation of K_2HgI_4 in the last experiment and the nearly equivalent amounts of free mercury and diallyl (*cf.* Oppenheim, *Ber.*, 1871, **4**, 671) lend support to this conjecture Hence reagents which act on organo-mercuric compounds in the cold and bring about "condensation" were next tried (Whitmore, "Organic Compounds of Mercury," p. 59). Sodium thiosulphate and alkaline sulphide solutions were found to have only very slight action on C_3H_5HgI, and the black insoluble products were only inorganic mercury compounds, and the solution appeared to contain no new organomercuric compound.

When strongly alkaline solution of sodium stannite was added to C_3H_5HgI suspended in water (*cf.* Dimroth, *Chem. Zentrl.*, 1901, I, 451 ; Whitmore, *loc. cit.*, p. 63), mercury separated immediately and an oily liquid with a very offensive smell was formed. The oily liquid was extracted with ether, the ethereal solution dried over $CaCl_2$, and the ether distilled off. A clear colourless liquid with a nauseating odour was obtained.

This product contains Hg, C and H, and it burns with a luminous flame forming yellow fumes of HgO. It is not spontaneously inflammable nor does it oxidise very rapidly in air, but mercury separates on standing at room temperature (30-35°). The liquid cannot be distilled even in nitrogen at less than 1 mm. pressure as it decomposes into mercury and diallyl.

The compound, freed from ether as far as possible, becomes viscous when cooled with ice and salt but it crystallises in long needles with solid carbon dioxide. It crystallises from ethereal solutions also when cooled with carbon dioxide snow. Attempts were made to purify the substance by crystallisation from ether at low temperatures using a specially designed all glass apparatus in a moisture-free nitrogen atmosphere. In each case, however, mercury began to separate before the last traces of ether had been removed. The composition of the substance, while still containing traces of ether, was determined and derivatives prepared.

Samples of the purest preparations obtained were drawn into weighed capillaries, before separation of mercury set in and analysed. The mercury was weighed as $HgCr_2O_7, 2C_5H_5N$, and the carbon and hydrogen were estimated by the ordinary methods. [Found : C, 26 37 ; H, 3·92 , Hg, 70·1. $Hg(C_3H_5)_2$ requires C, 25·49 ; H, 3·567 ; Hg, 70·99 per cent]. These results are low for mercury and rather high for C and H owing to traces of ether present. They are, however, sufficiently accurate to show that the substance is mercury diallyl. The yield is nearly quantitative

Mercury diallyl is soluble in ether, benzene and carbon disulphide but it is insoluble in absolute alcohol. On heating in a sealed tube in an atmosphere of nitrogen it decomposes into mercury and diallyl. Its density is 2·1.

On coming in contact with the skin, it causes painful blisters after a few hours. Even in red light it slowly decomposes depositing mercury. A moderately concentrated solution keeps for a few hours and it was used for the reactions described below.

Mercury dialkyls react with halogens, halogen hydracids, and mercuric halides as in

$$HgR_2 + X_2 \longrightarrow RHgX + RX$$
$$HgR_2 + HX \longrightarrow RHgX + RH$$
$$HgR_2 + HgX_2 \longrightarrow 2RHgX.$$

(Whitmore, " Organic Compounds of Mercury," Ch. III and Newton Friend, " Text Book of Inorganic Chemistry " Vol. XI, Goddard and Goddard, Ch. III). So if the substance is $Hg(C_3H_5)_2$, these reagents would all be expected to give C_3H_5HgI.

An alcoholic solution of iodide gave an immediate precipitate of glistening white crystals turning yellow on exposure to light. Recrystallised from alcohol they melted with partial decomposition at $133°$ and gave with Na_2SnO_2 the same liquid with the unpleasant smell. Very dilute HI also gave C_3H_5HgI dissolving in excess. HgI_2 also gave C_3H_5HgI, though in very small yield.

Action of Bromine on Mercury-Diallyl : Preparation of Allyl Mercuric Bromide.—Mercury diallyl inflames with liquid bromine. An ethereal solution of bromine gives a white shining crystalline precipitate. This product crystallises from alcohol in transparent silvery plates, melting with partial decomposition at $124-25°$. It sublimes at about $95°$. (Found : C, $11·11$; H, $1·53$; Br, $25·04$; Hg, $62·1$. C_3H_5HgBr requires C, $11·2$; H, $1·568$; Br, $24·86$; Hg, $62·4$ per cent). C_3H_5HgBr is soluble in ether, acetone, cabon disulphide and benzene. By the action of Na_2SnO_2, $Hg(C_3H_5)_2$ is formed. Very dilute HBr, excess of which is to be avoided, and also alcoholic $HgBr_2$ react with $Hg(C_3H_5)_2$ to form C_3H_5Hg Br.

Preparation of Allyl Mercuric Chloride.— Mercury diallyl inflames when dropped into chlorine gas With chlorine in carbon tetrachloride it gives an insoluble white compound which appears to be mercurous compound. Alcoholic $HgCl_2$ also gives a similar insoluble compound. Allyl mercuric chloride was prepared by the action of approximately 4% HCl on $Hg(C_3H_5)_2$. C_3H_5HgCl crystallises from alcohol, in glistening plates, melting with partial decomposition at $102-103°$. (Found : C, $13·22$; H, $1·89$; Cl, $12·82$; Hg, $72·4$. C_3H_5HgCl requires C, 12.99 ; H, $1·819$; Cl, $12·79$; Hg, $72·38$ per cent.) It sublimes above $80°$. It is soluble in acetone, ether, carbon disulphide, benzene and aqueous alcohol. Na_2SnO_2

solution gives $Hg(C_3H_5)_2$. The action of HCl on $Hg(C_3H_5)_2$ may be represented by

$$Hg(C_3H_5)_2 + HCl \longrightarrow C_3H_5HgCl + C_3H_6.$$

The gas evolved was identified as propylene. Bromination yields propylene dibromide, b.p. 142°. Strong solutions of HCl react with C_3H_5HgCl as

$$C_3H_5HgCl + HCl \longrightarrow C_3H_6 + HgCl_2$$

which is similar to the action of strong HI on C_3H_5HgI; (cf. Linnemann, *Annalen Suppl.*, 1865, **3**, 262).

An interesting gradation of properties is observed in the three allyl mercuric halides. The chloride, bromide and iodide melt with partial decomposition at 102-3°, 124-25°, and 133-35° respectively. They sublime at about 80°, 95°, and 100° respectively. Solubility in various solvents and stability towards light decrease from the chloride to the iodide. The chloride remains undecomposed without giving any smell even after weeks, whereas the iodide is turned yellow rapidly on exposure to light and gives off a penetrating smell, indicating partial decomposition, on keeping in the dark for a few hours. The bromide gives traces of insoluble matter on keeping for a few weeks indicating partial decomposition.

Potassium permanganate solution acts on mercury dialkyls forming the hydroxides (Seidel, *J. pr. Chem.*, 1814, **291**, 135)

$$HgR_2 + (O) + H_2O \longrightarrow RHgOH + ROH.$$

$Hg(C_3H_5)_2$ decolourises $KMnO_4$ precipitating MnO_2, but the filtrate does not contain C_3H_5HgOH, for, with halogen hydracids, it does not give allyl mercuric halides nor does it give mercury diallyl with Na_2SnO_2.

Probably the solution contains γ-hydroxymercuripropyleneglycol obtained by the oxidation of the double bond at the same time as the oxidation of the mercury diallyl. The salts of this base are known (cf. Whitmore, " Organic Compounds of Mercury," p. 133).

The author is deeply indebted to Professor Edward Barnes at whose suggestion the work was undertaken and under whose direction and guidance it was carried out.

ON THE BITTER PRINCIPLES OF *CITRUS DECUMANA*.

By (Miss) Asima Mookerjee.

Two bitter principles, isomeric with each other and having the formula, $C_{26}H_{30}O_8$, have been isolated from the seeds of *Citrus decumana*. One of these has proved to be identical with limonin, while the other appears to be a new compound and has been called *neolimonin*. Alkali treatment of neolimonin furnished hexahydrolimoninic acid and another compound, which may be identical with *isolimonin* originally described by Koller and Czerny A comparative study of the colour reactions of neolimonin, limonin and *isolimonin* has been made. Hexahydrolimoninic acid has been obtained in a crystalline form for the first time.

The bitter principles of Citrus seeds have been investigated rather extensively. As early as 1841 Bernay (*Annalen*, 1841, **40**, 317) isolated from the seeds of many species of Citrus (*C. aurantium*, Risso, *C. limonum*, Risso, and *C. bigardia*, Loisl) a very bitter substance which he named limonin. He erroneously thought it to be an alkaloid. Three years later Schmidt (*Annalen*, 1844, **51**, 388) showed that Bernay's limonin was not a basic substance and that it resembled columbin, isolated from the root of *Jateorrhiza palmata* by Wittstock (*Pogg. Ann.*, 1830, **19**, 298). Schmidt, moreover, found that limonin, $C_{22}H_{26}O_7$, (m.p. 242°) was physiologically inactive. Since then other workers have studied its properties and reactions (Paterno and Oglialoro, *Ber.*, 1879, **12**, 685; Peters and Frerich, *Arch. Pharm.*, 1902, **240**, 661).

Peters and Frerich purified limonin by alkali treatment and recorded the m. p. 275°. Recently Koller and Czerny (*Monatsh.*, 1936, **67**, 248; 1937, **70**, 26) have reported the results of a more elaborate investigation of limonin, $C_{23}H_{26}O_7$ (m. p. 280°) isolated from orange pips. They isolated a second bitter substance, $C_{23}H_{28}O_7$ (m. p. 264°), from the same source which they named *isolimonin*. Shortly thereafter Feist and Schulte (*Ber.*, 1936, **69**, 1322) isolated from lemon seeds a third bitter substance, named citrolimonin, m. p. 304°, for which they advanced the molecular formula $C_{26}H_{30}O_8$. Similarity in equivalent weight and specific rotation of citro-limonin and limonin have led Koller and Czerny to believe these two compounds to be identical, despite a considerable discrepancy in the reported melting points. Koller and Czerny suggested that the lower melting point

of their limonin might be due to the use of alkali during isolation and puri-
fication, a suggestion which the present worker has been unable to support
(*vide infra*).

In a recent communication Higby (*J. Amer. Chem. Soc.*, 1938, **60**, 3013)
reported the isolation of two bitter lactones, namely limonin, $C_{26}H_{30}O_8$
(m.p. 290°, decomp) from Valencia orange and *iso*limonin, $C_{26}H_{30}O_8$
(m.p. 264°, decomp.) from Washington Navel orange. From analytical and
other data he concluded that his limonin was identical with the citro-
limonin of Feist and Schulte and the limonin of Koller and Czerny. As
regards his *iso*limonin, Higby did not establish its identity with Koller
and Czerny's *iso*limonin but the similarity in melting point and other
properties was emphasised.

The present investigation has been undertaken with a view to isolate
the bitter principles of the seeds of a variety of *Citrus decumana* (N.O.
Rutaceæ), known locally as *Bátávi*. From the air-dried seeds two colourless
crystalline bitter substances, besides a thick pale yellow oil, have been iso-
lated. These bitter principles have been purified *without* treatment with
alkali and many of their properties have been studied. One of the consti-
tuents (m.p. 280°, decomp. ; yield 0.23%) has been found to be identical
with Higby's limonin by a direct comparison which has been made possible
through the kindness of Dr. R. H. Higby, to whom the authoress is greatly
indebted. The second bitter constituent (m.p. 240-42°, decomp. ; yield
0.15%) has been found to be a new compound and has consequently been
named *neolimonin*.
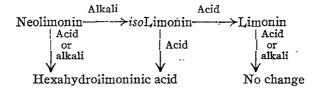
Neolimonin, $C_{26}H_{30}O_8$, $[\alpha]_D^{23} = -111°$ (acetone), yields a phenylhydra-
zone, m.p. 215-20°, whereas a yellow osazone, m.p. 221-25°, has been obtained
from *iso*limonin (Higby, *loc. cit.*). Neolimonin has no methoxy and
methylenedioxy groups. On acetylation neolimonin gives what is regarded
as an anhydrodiacetyl derivative (m.p. 219-20°, decomp.) whereas *iso*limonin
furnishes a diacetyl derivative, the m. p. of which has not been recorded
(Koller and Czerny, *loc. cit.*).

It has been observed by Higby that boiling hydrochloric acid converts
*iso*limonin into limonin and hexahydrolimoninic acid. Under similar ex-
perimental conditions neolimonin is partially converted into hexahydro-
limoninic acid. Alkali treatment, however, gives the same acid and another
neutral product, m. p. 262° (decomp.). The physical properties of the latter
agree with those of *iso*limonin which have been reported to melt at 264°,
(decomp.) (Higby) and 262-64° (decomp.) (Koller and Czerny). The

analytical data (C, 63·0 ; H, 7·0%), however, are not in agreement with those of *iso*limonin which requires C, 66·3 and H, 6·43 per cent. Further considerations about its molecular composition are postponed partly on account of the poor yield and partly for want of an authentic specimen of *iso*limonin of Koller and Czerny.

Hexahydrolimoninic acid was obtained by Higby as an amorphous, light coloured, globular aggregate, m. p. 175-77° and by Koller and Czerny as an amorphous substance which passed into crystalline state, m.p. 173°, on keeping in contact with water. It has now been found that the acid crystallises from acetone and has m. p. 201-3°. No marked difference in the analytical data between the two varieties are noticed and the m. p. of the amorphous variety is not depressed by admixture with the crystalline variety in equal proportions. Contrary to the experience of Koller and Czerny the methyl ester of hexahydrolimoninic acid has also been obtained in a crystalline condition, m. p. 173-4°.

Limonin remains unaffected by acid or alkali treatment and must, therefore, be considered as the most stable of the three compounds. The relationship between limonin, *iso*limonin and neolimonin is indicated below :

$$
\begin{array}{ccccc}
& \text{Alkali} & & \text{Acid} & \\
\text{Neolimonin} & \!\!\longrightarrow\!\! & iso\text{Limonin} & \!\!\longrightarrow\!\! & \text{Limonin} \\
\big|\ \text{Acid} & & \big| & & \big|\ \text{Acid} \\
\big|\ \text{or} & & \big|\ \text{Acid} & & \big|\ \text{or} \\
\big\downarrow\ \text{alkali} & & \big\downarrow & & \big\downarrow\ \text{alkali} \\
\text{Hexahydroiimoninic acid} & & & & \text{No change}
\end{array}
$$

Since *iso*limonin has a melting point intermediate between the melting points of limonin and neolimonin, it was thought that it might be a mixture of the last two compounds. The presence of one-third molecule of alcohol of crystallisation in *iso*limonin, on this assumption, would correspond to a mixture of limonin and neolimonin in the ratio of 6:1. In fact a mixture of limonin (6 parts) and neolimonin (1 part) melted indefinitely between 233° and 271° and the mixture on crystallisation gave products which melted at 256-74° (first crop), 253-72° (second crop) and 248-52° (third crop). No product with a sharp m.p. of 262° could be isolated. Therefore, *iso*limonin cannot be regarded as a mixture of limonin and neolimonin. It has, moreover, been observed that the m.p. of neolimonin is depressed by admixture either with limonin or *iso*limonin. The colour reactions of the three compounds, as given below, also prove that they are different from one another.

Colour Reactions of Neolimonin, isoLimonin and Limonin.

Reagents or Reactions.	Limonin.	Neolimonin.	*iso*Limonin.
Concentrated sulphuric acid	Deep red soln.	Same	Same
Concentrated sulphuric acid + anisaldehyde	Purple	Purple	At first a pinkish tinge turning red
Concentrated sulphuric acid + $K_2Cr_2O_7$	Red, then pale yellow, finally green	Red, then quickly green.	Red, then slowly green
Erdmann's reagent	Yellow, then almost colourless	Red	Deep red
Frohde's reagent	Red, then black	Yellow, then red	Red, and finally black
Mandelin's reagent	Red, then deep green	Greenish yellow, green, then rapidly yellow	Yellow with greenish tinge, then deep yellow, finally black
o-Dinitrobenzene (alkaline)	Dirty purple, then red	Same	Same
Liebermann's reaction	(i) H_2SO_4-layer pale orange (ii) CCl_4-layer : colourless	(i) Yellow (ii) Pink	(i) Purple, then red (ii) Colourless
Liebermann—Burchard's reaction	$CHCl_3$-layer : colourless (ii) H_2SO_4-layer : pink, yellow, then black	(i) Same (ii) Purple, then orange	(i) Same (ii) Yellow, then red
Salkowiski's reaction	(i) H_2SO_4-layer : yellow (ii) $CHCl_3$-layer : colourless	Same	Same
Lifschutz reaction	(i) H_2SO_4-layer : pink (ii) $CHCl_3$-layer : purplish (Pink ring at junction)	(i) Same (ii) Same	(i) Same (ii) Same
Rosenheim's reaction	(i) H_2SO_4-layer : colourless (ii) $CHCl_3$-layer : colourless	Same	Same

It is interesting to note that Higby had obtained a compound, m.p. 240-42° (decomp.), from Navel orange, which he considered to be impure *iso*limonin and obtained pure *iso*limonin from it after treatment with alkali. It has been established in course of the present investigation that neolimonin

undergoes transformation into *isolimonin* under the influence of alkali. It is, therefore, very likely that *isolimonin* is not present as such in Navel orange, but is a secondary product derived from neolimonin. The same remark also applies to the occurrence of *isolimonin* in orange seeds as observed by Koller and Czerny. This hypothesis, however, needs further verification.

The structural relationship between limonin, neolimonin and *isolimonin* is not very clear. Although limonin has been subjected to chemical investigation, for nearly a century, no structural formula for the substance has been advanced. Recent workers, however, agree that it contains two lactone groups, and Koller and Czerny suggested that limonin may be related to columbin and hence to cardiac aglucones. The present worker has been able to account for many of the reactions of limonin on the basis of this hypothesis, but rigid chemical evidence has yet to be adduced in its support.

EXPERIMENTAL.

Isolation of Limonin and Neolimonin.—The seeds of *C. decumana* (2 kg.), collected in the locality, were coarsely powdered and extracted with petroleum ether (b. p. 40-60°) in a Soxhlet for 6-8 hours to remove the major part of the oil, and then extracted with benzene during 24 hours. The pale yellow benzene extract was concentrated on the water-bath under reduced pressure to about 100 c.c., when crystals of limonin and neolimonin separated out. The crude product (12 g.) was collected, washed with cold benzene (40 c.c.) to remove fatty matters, and then slowly crystallised from acetone (100-150 c.c.). The crystals consisted of opaque star-shaped aggregates of limonin and transparent rods of neolimonin. The two types of crystals were separated from each other mechanically, and the two fractions were repeatedly crystallised from acetone till the m.p. of limonin (yield 4·5 g.) became constant at 230° and that of neolimonin (yield 3 g.) at 240-42°.

Limonin crystallises from acetone in thick rhombic plates or from alcohol in thin shining flakes. It crystallises from acetic acid with one molecule of acetic acid, although it has no tendency to combine with alcohol or acetone. A chloroform solution of limonin easily discharges the colour of bromine. Limonin also combines with one molecule of phenyl-hydrazine.

Neolimonin dissolves freely in chloroform and pyridine; it is fairly soluble in acetone but sparingly in alcohol, and insoluble in ether, petroleum ether and water. The crystals are transparent when crystallised

2

from acetone. They become opaque when kept exposed to air for a few
days evidently due to the loss of acetone of crystallisation. Acetone is
completely removed on drying at 120-25° in *vacuo* over P_2O_5 for a few
hours. Alcohol of crystallisation is, however, not lost so easily. A specimen,
crystallised from alcohol and dried for 3 hours at 100° in *vacuo*, gave on
analysis: C, 63·50 ; H, 7·00. $C_{26}H_{30}O_8$, $2C_2H_5OH$ requires C, 64·03 ; H, 7·4
per cent. Another specimen, crystallised from acetone, was dried to constant
weight in *vacuo* at 120-25°. (Found : loss in weight, 10·93. $C_{26}H_{30}O_8$,
Me_2CO requires 10·98 %. Found in a dry specimen : C, 65·80 ; H, 6·7.
$C_{26}H_{30}O_8$ requires C, 66·30 ; H, 6·43 per cent).

Neolimonin (0·2973 g.), dissolved in acetone (50 c.c.), showed a rotation
of −0·66° in 1 dcm. tube at 33°. Hence $[a]_D^{33} = -111°$.

Acetylation of Neolimonin.—A mixture of neolimonin (0·1 g.), acetic
anhydride (2 c.c.) and a drop of pyridine was gently boiled for 4 hours.
The liquid products of the reaction were removed under reduced pressure
and the brown residue taken up with acetone, charcoaled and filtered.
After a week, the solution, which exhibited a green fluorescence deposited
a small quantity of pale yellow plates, which became colourless after three
crystallisations from acetone, and had m.p. 219-20°. (Found in sample dried
in *vacuo* over P_2O_5 at 100° for 3 hours: C, 67·34 ; H, 6·5. $C_{30}H_{32}O_9$
requires C, 67·16 ; H, 6·0 per cent).

Phenylhydrazone of Neolimonin.—Neolimonin (0·2 g.) was refluxed
in alcoholic solution with freshly distilled phenylhydrazine (0·3 g.) and
glacial acetic acid (0·3 c.c.) on the water-bath for 3 hours. The yellow
solution was freed from alcohol under diminished pressure and the residue
taken up with 80% alcohol (15 c.c.) and concentrated. The yellow amorphous
precipitate was collected next day and washed with cold alcohol (20 c c.),
m.p. 215-20°. (Found in specimen dried at 120-25° for 3 hours in *vacuo*
over P_2O_5 : N, 4·60. $C_{32}H_{36}O_7N_2$ requires N, 5·00 per cent).

Action of Hydrochloric Acid on Neolimonin.—Pure neolimonin (0·7 g.),
dissolved in acetone (35 c.c.) was refluxed with 6N-hydrochloric acid (7 c.c.)
on the water-bath for 6 hours. After neutralisation with lead carbonate
the solution was filtered, concentrated, diluted with water and again heated
when a brown viscous mass separated out. This was collected and after
treatment with sodium bicarbonate solution, was crystallised from acetone
and found to be unchanged neolimonin. The bicarbonate solution was
acidified with hydrochloric acid, the precipitate was collected, washed with
a little ice-cold water and after drying in a desiccator (calcium chloride),
was purified by repeated dissolution in sodium bicarbonate and precipitation
with hydrochloric acid; m.p. 175-77°. (Found in a specimen dried at 100°

for 3 hours in *vacuo* over P_2O_5 : C, 62·60 ; H, 7·8. $C_{26}H_{38}O_9$ requires C, 63·1 ; H, 7·69 per cent). The hexahydrolimoninic acid described above (0·0616 g.), dissolved in acetone (25 c.c.), showed a rotation of —0·085° in a 0·5 dcm. tube. Hence $[\alpha]_D^{33} = -69°$. Higby records $[\alpha]_D^{22} = -70°$ for the amorphous acid.

Crystalline Hexahydrolimoninic Acid.—The above acid was repeatedly crystallised from acetone when it formed colourless shining rods, m.p. 201-3°. (Found in a specimen dried for 3 hours at 135-40° in *vacuo* over P_2O_5 : C, 63·42 ; H, 7·33. $C_{26}H_{38}O_9$ requires C, 63·10 ; H, 7·69 per cent). The crystalline acid showed $[\alpha]_D^{30} = -74.3°$ (acetone).

Action of Alkali on Neolimonin.—A clear solution of neolimonin (0.18 g.) in aqueous potassium hydroxide (10 c.c. of 13%) was acidified with hydrochloric acid after standing for 2 hours at room temperature. The precipitate was collected, and washed with ice-cold water, when a part (0.09 g.) became insoluble in bicarbonate solution. From the filtrate an amorphous precipitate (0.08 g.) was isolated after acidification. Purified by dissolution in sodium bicarbonate and acidification with hydrochloric acid, and finally by crystallising from acetone (till the m.p. became constant) colourless needles (identified as hexahydrolimoninic acid), m.p. 201-3°, were obtained. (Found in specimen dried at 135-40° for 2 hours in *vacuo* over P_2O_5 : C, 63·42 ; H, 7·33. $C_{26}H_{38}O_9$ requires C, 63·10 ; H, 7·69 per cent).

The insoluble residue (0·09 g., referred to above) was thrice crystallised from alcohol when thick plates, m.p. 262° (decomp.) (unaltered by further crystallisation) were obtained. When heated to 140° it turned opaque, became an opaque powder at 225-235° and finally melted at 262° with decomposition. Crystallised from a mixture of pyridine and benzine it had the same m.p., but did not show the heat changes as recorded above showing that the former specimen had alcohol of crystallisation. Dried to constant weight in *vacuo* at 135° it gave C, 63·0 ; H, 7·0 per cent. This substance may be *isolimonin*.

Methyl Ester of Hexahydrolimoninic Acid.—Hexahydrolimoninic acid (0.04 g.), dissolved in pure methyl alcohol, was treated with an excess of ethereal diazomethane and the mixture left for 20 hours at room temperature. The residue left after removal of the solvents crystallised from benzene, when colourless transparent plates, m.p. 173-74°, were obtained. These, however, soon lost their transparency and became opaque apparently due to loss of solvent of crystallisation. Koller and Czerny had obtained an amorphous methyl ester of the acid, the m.p. of which has not been recorded.

Limonin.—Limonin, m.p. 280° (decomp.), isolated from *C. decumana* was dried at 120° for 3 hours in *vacuo* over P_2O_5. (Found : C, 65·87 ; H, 6·24. $C_{26}H_{30}O_8$ requires C, 66·30 ; H, 6·43 per cent). The substance (0·398 g.), dissolved in acetone (25 c.c.), showed a rotation of -3.54° in 1.89 dcm. tube at 33°, whence $[a]_D^{33} = -117°$. (Higby records -106°, -108° and -114° at 20.° in acetone depending upon the source of limonin). Mixed m.p. of limonin with Higby's compound was found to be 279-80° (decomp.).

Phenylhydrazone of Limonin.—Limonin furnished an amorphous red-dish phenylhydrazone, m.p. 250-55°, when the experimental conditions described under neolimonin phenylhydrazone were followed. (Found in a specimen dried for 2 hours at 120° in *vacuo* over P_2O_5 : N, 5·3. $C_{32}H_{36}O_7N_2$ requires N, 5.00 per cent).

Action of Hydrochloric Acid on Limonin. —Limonin (0.5 g.), dissolved in acetone (25 c.c.), was refluxed with 6N-hydrochloric acid (5 c.c.) for 6 hours on the water-bath. The solution was worked up as described before in the case of neolimonin. The crystalline precipitate (0.5 g.) in this case was entirely insoluble in sodium bicarbonate solution, and formed heavy plates, m.p. 280° (decomp.), after two crystallisations from acetone and was identified as unchanged material by a direct comparison.

Action of Alkali on Limonin.—Limonin (0.2 g.) was dissolved in potassium hydroxide (10 c.c. of 13%) and the clear solution kept for 48 hours. The precipitate (0·195 g.), obtained on acidifying the solution, did not dissolve at all in sodium bicarbonate solution, and the filtrate showed a blue fluorescence. The precipitate crystallised from alcohol in shining flakes, m.p. 280° (decomp.), not depressed by admixture with limonin.

KOSTANECKI-ROBINSON REACTION. PART III.
BENZOYLATION OF ORCACETOPHENONE
AND ITS MONOMETHYL ETHER.

By S. M. Sethna and R. C. Shah.

In continuation of the previous work orcacetophenone has been benzoylated giving 7-benzoyloxy-3-benzoyl-5-methylflavone. This on treatment with concentrated sulphuric acid gives 7-hydroxy-3-benzoyl-5-methyl-flavone which on treatment with alcoholic potash gives 7-hydroxy-5-methylflavone. A noteworthy point is the new technique for the stepwise elimination of O-benzoyl group and the C-benzoyl group in the γ-pyrone ring.

In continuation of the previous work (*J. Indian Chem. Soc.*, 1940, 17, 239, 487) orcacetophenone has been benzoylated. The reaction mixture after benzoylation is treated with petroleum ether and water to remove benzoic anhydride and sodium benzoate respectively when a product (*A*), $C_{20}H_{30}O_5$, is obtained. This on treatment with concentrated sulphuric acid gives an alkali-soluble product (*B*), $C_{23}H_{16}O_4$, which on treatment with alcoholic potash gives a product (*C*), $C_{16}H_{12}O_3$, with the loss of a benzoyl group. This product is 7-hydroxy-5-methylflavone (I, R=R′=H), prepared previously by Tambor (*Ber.*, 1908, 41, 793) by the condensation of orcaceto-phenone dimethyl ether with methyl benzoate and subsequent ring-closure of the β-diketone. He records the m.p. 297° for the flavone and 115° for its methyl ether. Our m.ps., however, are 312° and 122-23° respectively.

Thus the product (*A*), which is 7-benzoyloxy-3-benzoyl-5-methylflavone (I, R=R′=COPh), gives on treatment with concentrated sulphuric acid the product (*B*), 7-hydroxy-3-benzoyl-5-methylflavone (I,R=H; R′=COPh), which on treatment with alcoholic potash gives 7-hydroxy-5-methylflavone of Tambor (*loc. cit.*).

The monomethyl ether of orcacetophenone on similar benzoylation and subsequent treatment of the reaction product with petroleum ether and water gives 7-methoxy-3-benzoyl-5-methylflavone, identical with the methyl ether of (I,R=H; R′=COPh). This on treatment with alcoholic potash gives 7-methoxy-5-methylflavone, identical with the methyl ether of (I,R=R′=H).

The procedure generally adopted in working up the product obtained on the aroylation of o-hydroxy-ketones is the treatment of the reaction mixture with alcoholic potash. This leads generally to the removal of both the O-aroyl group and the C-aroyl group in the pyrone ring and the 3-aroyl-flavones are not generally capable of isolation. Some workers have,

however, been able in a few cases to isolate 3-benzoylflavones by modifica-
tions of the usual procedure of working up the reaction products or
changing the conditions of reaction   (Algar, McCarthy and Dick, *Proc.
Roy. Irish Acad*, 1933, **41B**, 155 ; Baker, *J. Chem. Soc* , 1933, 1381 ; Suga-
sawa, *ibid.*, 1934, 1483, Rangaswami and Seshadri, *Proc. Indian Acad. Sci.*,
1939, **10A**, 6).

The experimental technique, followed here, of treating the reaction
mixture after benzoylation with petroleum ether and water, to remove
benzoic anhydride and sodium benzoate respectively can be of great value
in the isolation of flavones with both the *O*- and the *C*- benzoyl groups
intact.   The *O*-benzoyl group can be then smoothly removed by the use of
concentrated sulphuric acid leaving the 3-benzoyl group intact.   The
method promises to be of general use and preliminary experiments with
other *o*-hydroxy-ketones justify this expectation.

(I)

EXPERIMENTAL.

*Benzoylation   of   Orcacetophenone :   7-Benzoyloxy-3-benzoyl-5-methyl-
flavone* (I, R=R′=COPh).—Orcacetophenone (5 g.), sodium benzoate
(15 g.) and benzoic anhydride (50 g.) were heated in a 250 c.c. round-
bottomed flask in an oil-bath at 180-190° for 8 hours. The compact mass
obtained was ground up and refluxed repeatedly with petroleum ether
(b.p. 40-60°) and filtered each time till the benzoic anhydride was removed.
The product was dried and then ground up with excess of water to
remove sodium benzoate.   The residue was then crystallised from rectified
spirit in slender shining needles (4 g.), m. p. 172-73°. The product is
insoluble in alkali and gives no colouration with alcoholic ferric chloride.
(Found : C, 78·0 ; H, 4.4. $C_{30}H_{20}O_5$ requires C, 78·3 ; H, 4·3 per cent).

7-Hydroxy-3-benzoyl-5-methylflavone (I, R=H ; R′=COPh).—The
above condensation product (I, R=R′=COPh ; 2 g.) was shaken up with
concentrated sulphuric acid (15 c.c.) and kept for 4 hours. The product,
obtained on adding the reaction mixture to water, was crystallised from
rectified spirit in rectangular prisms (1 g.), m.p., 282-83°. The product is
soluble in caustic alkalis without any fluorescence. It also gives no fluore-
scence with concentrated sulphuric acid. (Found: C, 77·4 ; H, 4·8.
$C_{23}H_{16}O_4$ requires C, 77·5 ; H, 4·5 per cent).

The *acetyl derivative*, prepared as usual with sodium acetate and acetic anhydride, was crystallised from alcohol in rectangular prisms, m.p. 171-73°. (Found : C, 75·0 ; H, 4·7. $C_{25}H_{18}O_5$ requires C, 75·4 ; H, 4·5 per cent).

The *methyl ether*, prepared as usual with potassium carbonate and methyl iodide, was crystallised from rectified spirit in clusters of tiny needles, m.p. 186-87°. (Found : C, 77·6 ; H, 5·0. $C_{24}H_{18}O_4$ requires C, 77·8 ; H, 4 9 per cent'.

7-Hydroxy-5-methylflavone.—Debenzoylation did not take place on keeping 7-hydroxy-3-benzoyl-5-methylflavone with 10% sodium hydroxide for 60 hours. It was, however, effected by heating the benzoyl derivative with alcoholic potash. 7-Hydroxy-3-benzoyl-5-methylflavone (0·5 g.) was re-fluxed with alcoholic potash (10% ; 25 c.c.) for ½ hour. The excess of alcohol was distilled over and the reaction mixture acidified with hydrochloric acid. The product obtained was crystallised from rectified spirit in tiny needles (0.2 g.), m.p. 312°. Tambor (*loc. cit.*) gives m.p. 297°. The product gives bluish fluorescence with concentrated sulphuric acid and caustic alkalis. (Found : C, 76·1 ; H, 4·7. $C_{16}H_{12}O_3$ requires C, 75·2; H, 4·8 per cent).

7-Benzoyloxy-3-benzoyl-5-methylflavone was similiarly debenzoylated to 7-hydroxy-5-methylflavone.

7-Methoxy-5-methylflavone, prepared with dimethyl sulphate and alkali, was crystallised from rectified spirit in needles, m.p. 122-23°: Tambor (*loc. cit.*) gives m.p. 115°.

Benzoylation of Orcacetophenone Monomethyl Ether : 7-Methoxy-3-benzoyl 5-methylflavone.—Orcacetophenone monomethyl ether (2 g.), sodium benzoate (6 g.) and benzoic anhydride (20 g.) were heated for 7 hours at 180-90°. The product, obtained on treatment with petroleum ether and water as above, was crystallised from rectified spirit in clusters of tiny needles (0·6 g.), m.p. 186-87°. Mixed m.p. with the methyl ether of 7-hydroxy-3-benzoyl-5-methylflavone, described before, was not depressed.

On refluxing with alcoholic potash 7-methoxy-5-methylflavone was obtained as shown by direct comparison with the same.

Further work on the application of this method for the isolation of 3-aroyl-flavones is in progress. Experiments are also in progress to investigate the use of various other solvents in place of petroleum ether. All the analyses are microanalyses.

MAGNETIC SUSCEPTIBILITY AND OPTICAL ROTATORY POWERS OF p-HYDROXY-α-NAPHTHYLIMINOCAMPHOR.

BY MAHAN SINGH AND ARJAN SINGH

The magnetic susceptibility and rotatory powers of p-hydroxy-α-naphthylimino-camphor have been described The two forms of the compound have different suscep-tibilities which suggest that the differences are not due to the size of the aggregate of the molecules or stereoisomerism, but probably due to the difference in the consti-tutions.

Aryl derivatives of iminocamphor (Forster and Thornley, *J. Chem. Soc.*, 1909, **95**, 944 ; Singh and collaborators, *ibid.*, 1919, **115**, 566; 1920, **117**, 980 ; 1599) with a few exceptions exist in one form only, though Singh and Rai (*J. Indian Chem. Soc*, 1926, 389) have pointed out that these compounds by virtue of their containing an azethenoid group are capable of existing in two stereoisomeric forms.   Singh and Singh (*J. Indian Chem. Soc.*; 1935, **12**, 768) have prepared p-dimethylamino- and p-diethylamino-phenyliminocamphors, which are phototropic and the two forms show different rotatory powers. It is supposed that the substances exist in stereoisomeric forms.

p-Hydroxy-α-naphthyliminocamphor exists in two forms (red and light orange). The red form, prepared by crystallising from alcohol, is converted into the light orange form at 132-135°. This thermotropic change may be due to one of these causes; (i) a change in the size of the aggregate of the molecule, (ii) or to geometrical isomeric change as suggested by Singh and Singh (*loc.cit*), and (iii) constitutional change.

To decide this we have determined the magnetic susceptibilities of the two forms on a modified form of a Guoy's balance The values are:- -6.58×10^{-7} for the red and -6.46×10^{-7} for the light orange.

Bhatnagar, Kapur and Hashmi (*J. Indian Chem. Soc.*, 1938, **15**, 573) as the result of their study of the magnetic susceptibilities of phototropic compounds have come to the conclusion that the susceptibility value of the compound before and after exposure to light would remain the same if the phototropic change is not accompanied by any change in the crystal structure or a change in the constitution.

Again Bhatnagar, Mathur and Neogi (*Z. Physik.*, 1930, **69**, 373) have shown that the difference in the magnetic susceptibilities of the geometrical isomerides is negligible being of the order 0.032×10^{-7} to 0.052×10^{-7}. The susceptibility values of the two forms of p-hydroxy-α-naphthyl-

iminocamphor, however, differ by 0.120×10^{-7}, showing thereby that the thermotropic change from red to light orange is neither due to the change in the size of the aggregate of the molecule nor to the geometrical isomerism. If the constitution of the two varieties be represented by the following formulae then the net change in the mass susceptibility value of the compounds due to the various constitutional changes works out to be 0.121×10^{-7}, which agrees remarkably well with the experimental value.

$$C_8H_{14} \begin{array}{c} C=N-\langle\quad\rangle OH \\ | \\ C=O \end{array} \qquad -6.58 \times 10^{-7}$$

$$C_8H_{14} \begin{array}{c} C-N=\langle\quad\rangle=O \\ \| \\ C-OH \end{array} \qquad -6.46 \times 10^{-7}$$

Both the forms were examined polarimetrically in various solvents. The light orange form shows mutarotation in aniline, methyl alcohol and ethyl alcohol. The final value of the light orange form is the same as that of the red form and it appears that this is the rotatory power of the equilibrium mixture. There is no mutarotation in ethyl alcohol if 2-3 drops of pyridine are added and it seems that the equilibrium is established within a very short time. The rotatory powers of both the forms in nitrobenzene are almost identical and the light orange form shows no mutarotation.

E X P E R I M E N T A L

Condensation of Camphorquinone and 1 : 4-*Aminonaphthol Hydrochloride.* —Equimolecular quantities of camphorquinone and 1 : 4-aminonaphthol hydrochloride with fused sodium acetate were heated on a water-bath at 45-50° for $\frac{1}{2}$ hour. It was then extracted with alcohol and precipitated with water and the process repeated several times till the product was bright orange in colour free from tarry matter. The precipitate was crystallised from warm alcohol as bright red crystals, melting at 231° but with a change to light orange colour at 132-135°. It crystallised from hot alcohol as deep red crystals with blackish tinge. On spontaneous crystallisation both the varieties separated side by side and were mechanically separable.

At a slightly higher temperature (50-65°) the yield decreases considerably, most of it changing to a black product and finally at a temperature of 80°, the whole product reduces to a black tarry matter. (Found : N, 4 86. $C_{20}H_{23}O_2N$ requires N, 4. 56 per cent).

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1 : 4-Aminonophthol was prepared in good yield by reducing benzene-azonaphthol with sodium hydrosulphite ("Organic Syntheses" Vol. III). Attempts to prepare it by the reduction of *p*-sulphobenzene-azonaphthol with stannous chloride (Barnett, Preparation of Organic Compounds, 191) yielded resinous tarry matter.

The rotatory powers were determined in the usual way in a 2-dcm tube with the exception of aniline in the case of red form where 1 dcm tube was used.

Red form

Solvents	Conc. g/25 c.c.	α_D.	$[\alpha]_D$.
Aniline	0.0212	1·20°	1415°
EtOH	0.0100	1·08	1350
Me₂CO	0.0114	1·22	1337
MeOH	0.0100	0·98	1225
Nitrobenzene	0.013	1·19	1144

Light Orange form

Aniline	0.0140	1·80	1608
(after 21 hours)		1·62	1432
EtOH	0.0142	1 63	1435
(after 9 hours)		1·46	1285
EtOH	0.0100	1·05	1312
In the presence of 2-3 drops of pyridine			
MeOH	0.106	1·16	1368
(after 24 hours)		1·04	1226.4
Nitrobenzene	0.0100	0·95	1187

The rotatory powers of *p*-hydroxy-phenyliminocamphor were determined in the following solvents for the sake of comparison.

Aniline	0.0202	2·75°	1701°
Nitrobenzene	0.0217	2·43	1393

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A NEW SYNTHESIS OF HEXAHYDRO*ISO*PHTHALIC ACID.

By Phanindra Chandra Dutta.

A new method for the synthesis of stereoisomeric hexahydro*iso*phthalic acid has been described.

The condensation of ethyl oxalate with systems like ·
$$-CH_2-CH=CH-X(X=CO\ ;\ CO_2Et,\ C\equiv N),$$
described by Lapworth (*J. Chem. Soc.*, 1901, **79**, 1265), has undergone considerable modification recently largely due to the work of Kuhn and co-workers (*Ber.*, 1936, **69**. 1757, 1979 ; *cf.* Pedlar Memorial Lecture, *J. Chem. Soc.*, 1938, 610). Borsche (*Annalen*, 1934, **512**, 97) has condensed unsaturated nitriles like acrylonitrile and crotononitrile with oxalic ester in the presence of two molecules of potassium ethoxide, but so far no cyclic system has been studied in detail. *o*-Methyl*cyclo*hexanone has been converted into the related unsaturated nitrile by the method of Linstead (*J. Chem. Soc.*, 1936, 482). This was presumably a mixture of Δ^1-and Δ^6-forms. This was condensed with ethyl oxalate in presence of sodium ethoxide, when as has been shown by Lapworth (*loc. cit.*), the Δ^1-form alone reacts. With potassium ethoxide, the Δ^6-form also reacts (Borsche, *Ber.*, 1932, **68**, 865).

Δ^6-form　　　　　　　　　　　Δ^1-form

(I)　　　　　　　　　　　　　　　　(II)

To maintain the homogeneity of the product, sodium ethoxide has been used. The oxalo derivative (II, R=CO·CO_2Et) has been isolated from the alkaline solution in the form of colourless needles. Attempts to drive off carbon monoxide by heating up to 230° failed, the substance distilling smoothly in vacuum proving its unusual stability.

Similarly Δ^1-*cyclo*hexene has been condensed with oxalic ester under identical conditions to give (III, R=Et).

CH₂
H₂C C·CN
H₂C CH
CH
|
CO·CO₂R

(III)

CH₂
H₂C CH·CO₂Et
H₂C CH₂
CH
|
CO₂Et

(IV)

On hydrolysis with methyl alcoholic potassium hydroxide the correspon-
ding acid (III, R=H) is obtained in quantitative yield. Attempted
oxidation of the pyruvic acid derivative with hydrogen peroxide in alkaline
solution by the usual method is unsatisfactory and consequently it has been
oxidised in aqueous solution with hydrogen peroxide at 60°.

The unsaturated *cyclo*hexenecyano-acid has been reduced with sodium
amalgam and the reduced cyano-acid is isolated as the diethyl ester (IV).

After hydrolysis (IV) gives hexahydro*iso*phthalic acids. From the
mixture the *cis*-anhydride has been isolated by distillation in vacuum and
converted into the *cis*-hexahydro*iso*phthalic acid (*cf.* Perkin, *J. Chem. Soc.*,
1891, **59**, 808 ; Cook. *ibid.*, 1936, 68).

The choice of cyano*cyclo*hexene instead of ethyl tetrahydrobenzoate
(Kon, *J. Chem. Soc.*, 1933, 1631) for this series of reactions is due to the
fact that the reduction of the double bond in tetrahydro*iso*phthalic acid
is not possible with the usual reducing agents (Baeyer, *Ber.*, 1886, **19**, 1806 ,
Perkin, *loc. cit.*).

E X P E R I M E N T A L.

Ethyl (4-Methyl-3-cyano-Δ²-cyclohexenoyl)-formate (II, R=CO·CO₂Et).
—A solution of sodium (2·3 g.) in alcohol (35 c.c.) was cooled
in a freezing mixture and to this was added a cold mixture of
methylcyano*cyclo*hexene (12·1 g.) and ethyl oxalate (14·6 g.). The
mixture was thoroughly shaken and after allowing it to come to room
temperature gradually (15 hours) it was decomposed with ice. The neutral
portion was extracted with ether, and from the alkaline portion an oil
separated after acidification, which at once crystallised out in long needles,
m.p. 110°, yield 8·5 g. It had a characteristic smell and gave a deep
violet ferric reaction in alcoholic solution. It crystallised from alcohol in
needles with some of the solvent of crystallisation removable on prolonged
drying in vacuum. It was unusually stable to heat and distilled in vacuum

at 170°/9 mm. The distillate crystallised at once. (Found : N, 6·51, 6·52. $C_{12}H_{15}O_3N$ requires N, 6·34 per cent).

Ethyl (3-Cyano-Δ¹-cyclohexenoyl)-formate . (III, R=Et).—To a well cooled solution of sodium ethoxide (sodium 6·6 g, and alcohol, distilled over calcium, 86 c.c.), a similarly cooled mixture of cyano*cyclo*hexene (30 g.) and ethyl oxalate (42 c.c.) was added with thorough shaking. On working up in the usual way, a white crystalline substance was obtained. It was distilled at 156°/5 mm., the distillate crystallising in needles, m.p. 106°, yield 31 g. (Found : N, 6·9. $C_{11}H_{13}O_3N$ requires N, 6·7 per cent).

3-*Cyano*-Δ¹-cyclohexenoylformic *Acid* (III, R=H).—The above ester (31 g.), dissolved in methyl alcohol (120 c.c.), was shaken with a solution of sodium hydroxide (18 g.) in water (170 c.c.). After standing at the ordinary temperature for 2 days, the solution was heated on the water-bath for 1 hour and then acidified with ice-cold dilute sulphuric acid when a white crystalline precipitate separated, m.p. 197-99° (decomp.) after recrystallisation from dilute alcohol, yield 20 g. (Found : C, 60·6, H, 4·6. $C_9H_9O_3N$ requires C, 60·3 ; H, 5·0 per cent).

Ethyl Hexahydroisophthalate (IV).—The above acid (18 g.) was suspended in water (300 c.c.) and to this was added hydrogen peroxide (14 c.c. 28% by titration). The mixture was mechanically stirred and the temperature was gradually raised to 60°. The reaction started with frothing and after about 2 hours most of the acid went into solution and the temperature was maintained at 60°. The solution after filtration was thoroughly extracted with ether after saturation with ammonium sulphate. The ether extract was dried over sodium sulphate, whence a viscous mass was obtained. The yield of the acid from two experiments was 17 g.. This was reduced in a slightly acid solution with sodium amalgam (3%, 800 g.). The operation required about 8 hours and after isolation in the usual way, the yield of the reduced acid was 9 g. It was next esterified with a mixture of alcohol (50 c.c.) and sulphuric acid (12 c.c., d 1·84) and heated on the water-bath for 2 days. After isolation in the usual way the mobile oil had b.p. 124°/5 mm. (5 g.) together with a high-boiling residue. (Found : C, 63·1, 63·2 ; H, 8·8, 8·9. $C_{12}H_{20}O_4$ requires C, 63·1 ; H, 8·6 per cent).

Hexahydroisophthalic Acid.—Ethyl *cyclo*hexane-1 : 3-dicarboxylate (4 g.) was hydrolysed by refluxing with fuming hydrochloric acid (30 c.c) for 8 hours. The solution was concentrated to some extent when the acid separated as a sandy powder on cooling. It was dissolved in boiling water, charcoaled and concentrated on the water-bath and left aside for crystalli-

sation after the addition of a few drops of hydrochloric acid, m.p. 114-38$^\delta$, evidently consisting of a mixture of *cis*- and *trans*-forms (lit. m.p. 110-30°). (Found : C, 55·7 ; H, 6·5. $C_8H_{12}O_4$ requires C, 55·8 ; H, 6·9 per cent).

cis-Hexahydro*iso*phthalic acid was separated from the mixture by boiling the above acid (2 g.) with acetic anhydride (10 c.c.) for 5 hours and the residue left was sublimed in high vacuum when the anhydride of the *cis*-acid was obtained, m.p. 184° (lit. 185-86°), whence the *cis*-acid, m.p. 161°, was isolated (*loc. cit.*).

My grateful thanks are due to Prof. P. C. Mitter for his valuable suggestions, kind encouragement and interest during the course of these investigations.

STUDIES IN THE *CYCLOPENTANE* SERIES. PART I. SYNTHESIS OF 1-METHYLCYCLOPENTANE-1 : 2-DI-CARBOXYIC ACID IN *CIS-* AND *TRANS*-FORMS.*

By Phanindra Chandra Dutta.

A new method has been developed for the synthesis of substituted *cyclo*pentane rings and by this method 1-methyl-*cyclo*pentane-1 : 2-dicarboxylic acid has been syn-thesised in *cis-* and *trans*-forms. Their stereochemical properties have been studied in detail and their analogy with the two forms of *cyclo*pentane-1 : 2-dicarboxylic acids have been established.

This series of investigation was originally undertaken with a view to study the modes of formation and stereochemical properties of 1-methyl *cyclo*pentane-1 : 2-dicarboxylic acid (I), so that ultimately Wieland's acid (II), obtained by the oxidation of sterol and bile acids (*Z. physiol. Chem.*, 1924, **134**, 276), may be synthesised.

(I)   (II)

As a reference compound, the acid (I) has been prepared from ethyl 2-methyl*cyclo*pentanone-2-carboxylate by a method, which is, however, identical with that used by Linstead in the preparation of the corresponding *cyclo*hexane analogue. Ethyl 2-methyl*cyclo*pentanone-2-carboxylate has been converted into the cyanohydrin (III) with liquid hydrocyanic acid and this, on dehydration with thionyl chloride and pyridine, gives the unsaturated ester (IV, R=CN) (containing much dissolved sulphur, which is removed by boiling with precipitated copper in benzene solution.) It undergoes hydrolysis to the unsaturated acid (IV, R=COOH) and this, on reduction with sodium amalgam gives only the *trans*-form of the acid (I), m. p. 142°.

(III)   (IV)

* A preliminary note appeared in *Science and Culture*, 1940, **6**, 560.

Attention was then directed to its synthesis from open-chain compounds with the proper substituents. β-Ethoxyethyl iodide has been condensed with sodioacetoacetic ester to give ethyl γ-ethoxy-acetobutyrate and this on hydrolysis gives γ-ethoxypropylmethyl ketone (V). The cyanohydrin of the latter is condensed with sodiocyanoacetic ester (Thorpe and Higson, *J. Chem. Soc.*, 1906, **89**, 1455) and the ethoxydi-cyano-ester (VI) is isolated as a viscous liquid.

$$\begin{array}{ccc} \text{CH}_3 & \text{CH}_2 & \text{Br·(CH}_2)_3\text{·C·R·CO}_2\text{Et} \\ >\text{CO} & \text{H}_2\text{C} \quad \text{C} < \overset{\text{Me}}{\text{CN}} & | \\ \text{CH}_2 & \text{H}_2\text{C} \quad \text{CH(CN)—CO}_2\text{Et} & \text{Br} \\ | & \text{OEt} & \text{(VII)} \\ \text{CH}_2\text{—CH}_2\text{OEt} & & \\ \text{(V)} & \text{(VI)} & \end{array}$$

The latter (VI) has also been prepared in a very good yield by the addition of hydrogen cyanide to ethyl α-cyano β-(γ-ethoxypropyl)-crotonate (*cf.* Hope and Sheldon, *J. Chem. Soc.*, 1922, **121**, 2226; Cope, *J. Amer. Chem. Soc.*, 1937, **59**, 2327).

Attempted cyclisation of (VI) to (I) by heating with fuming hydrochloric acid furnishes a chlorinated acid instead of the desired *cyclo*pentane-acid. Simonsen (*J. Chem. Soc.*, 1909, **95**, 1171) converted methoxy-methylene-dimalonic ester into *cyclo*butane-1 : 3-dicarboxylic acid.

The hydrolysis of CN in (VI) to carbethoxy did not prove successful. But (VI) gives after hydrolysis and esterification, ethyl α-methyl-α-(γ-ethoxypropyl)-succinate.

Ethyl δ-bromo-α-carbethoxyvalerate (*Biochem. Z.*, 1930, **226**, 228) has been hydrolysed with hydrobromic acid and the semi-solid mass, so obtained, is treated with thionyl chloride and brominated *in situ* and ethyl $\alpha\delta$-dibromovalerate (VII, R=H), after interaction with sodiocyanoacetic ester gives (VIII) in very good yield, which has been obtained by Fuson (*J. Amer. Chem. Soc.*, 1938, **60**, 1237) in a different manner. On hydrolysis it gives crude *trans-cyclo*pentane-1 : 2-dicarboxylic acid and the conversion of the *cis*-form has been accomplished through its anhydride (Perkin, *loc. cit.*).

$$\begin{array}{cc} \text{CH}_2 & \text{CH}_2 \\ \text{H}_2\text{C} \quad \text{CH·CO}_2\text{Et} & \text{H}_2\text{C} \quad \text{C(Me)—CO}_2\text{Et} \\ \text{H}_2\text{C—C} < \overset{\text{CN}}{\text{CO}_2\text{Et}} & \text{H}_2\text{C—C} < \overset{\text{CN}}{\text{CO}_2\text{Et}} \\ \text{(VIII)} & \text{(IX)} \end{array}$$

Similarly, from ethyl methylmalonate and trimethylene bromide, ethyl γ-bromopropylmethylmalonate has been isolated in moderate yield. The latter, on hydrolysis with hydrobromic acid, gives the corresponding bromo-acid (*i.e.* γ-bromopropyl methyl malonic acid), probably contaminated with the related lactone. On treatment with phosphorus pentabromide and bromine and subsequent addition of alcohol, ethyl αδ-dibromo-α-methyl valerate (VII, R=Me) has been isolated· This on treatment with sodic-cyanoacetic ester gives the corresponding *cyclo*pentanecyano-ester (IX) in 89% yield. It is hydrolysed with concentrated hydrochloric acid to the pure *trans*-acid (I), m.p. 143°·

It may be noted that the appearance of the contiguous carboxyl groups in *cyclo*paraffin dibasic acids assume *cis*- configuration in *cyclo*butane series (Perkin, *J. Chem. Soc.*, 1894, **65**, 583), a mixture of *cis*- and *trans*-forms in *cyclo*hexane series (*cf.* Fuson, *loc. cit.*), and *trans*-configuration in the *cyclo*pentane series, which is of particular interest in this investigation.

When the cyano-ester (X) is heated in a sealed tube with concentrated hydrochloric acid, it is hydrolysed and decarboxylated to a mixture of *cis*- and *trans-cyclo*pentane acids (I). The crude product is treated with acetic anhydride, whereby the anhydride of the *cis*-acid is obtained as a gelatinous mass, b. p. 101°/4 mm., whence the *cis*-acid is obtained as clusters of small cubes, m.p. 124-26°. The range in m.p. indicates the partial formation of the anhydride. The *cis*- acid can also be obtained by heating the *trans*-acid with acetic anhydride and then distilling under reduced pressure, when a small amount of the anhydride is obtained as the distillate whence the acid can be isolated·

If the *trans*-acid is heated with hydrochloric acid at 190-200°, there is an appreciable conversion of the *trans*- into the *cis*- variety, but the reverse change can not be brought about. The method of analysis is, however, crude, depending mainly on the change in melting points and not on thermal analysis. Special interest attaches to the latter observation in connection with the synthesis of Wieland's tricarboxylic acid (II), where the carboxyl groups occupy *trans*-configuration.

It may be of interest to draw attention to the physical properties of the *trans*- and *cis- cyclo*pentane- 1- methyl- 1 : 2-dicarboxylic acids with the isomeric forms of *cyclo*pentane-1 : 2-dicarboxylic acids. The *cis*-variety crystallises in small cubes, m.p. 142°, whilst the *trans*-variety melts at 161° and crystallises in plates. The higher m.p. and lesser solubility are associated with the *trans*-acid, whilst lower m.p. and greater solubility in water are the properties of the *cis*-acid in this series as in others, such as *cis*- and *trans- cyclo*pentane- 1 : 2-dicarboxylic acids.

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Linstead has assigned definite structures to the two forms of *cyclo*hexane-1-methyl-1 : 2-dicarboxylic acids from similar considerations of physical properties alone.

<center>E X P E R I M E N T A L.</center>

*Ethyl 1-Methyl*cyclo*pentane-2-cyanohydrin-1-carboxylate* (III).—Hydrocyanic acid, generated from potassium cyanide (37 g.) and dilute sulphuric acid (37 c.c. in 40 c.c. of water), was passed into well cooled methyl-*cyclo*pentanone-carboxylic ester (25 g), to which a drop of potassium cyanide solution was added as a condensing agent. After standing overnight at 0°, a few drops of ice-cold dilute sulphuric acid were added and a current of air blown through the liquid to remove excess of hydrocyanic acid gas. The mixture was diluted, extracted with ether, dried and distilled in vacuum after the addition of a drop of sulphuric acid, b.p. 122°/4 mm., yield 24 g. (Found : N, 6·7. $C_{12}H_{15}O_3N$ requires N, 7·1 per cent).

1-*Methyl*-1-*carbethoxy*-2-cyclo*penten-2-nitrile* (IV, R=CN).—To a cooled mixture of the cyanohydrin (24 g.) and pyridine (22 g.) was added thionyl chloride (17 g.) drop by drop. After standing overnight the mixture was heated on the steam-bath for 2 hours. The supernatant clear liquid was extracted with dry ether and the plastic mass left was decomposed with ice and then thoroughly extracted with ether. The combined ethereal extract was washed with acid and alkali, dried and distilled in vacuum. The distillate contained much sulphur, which was removed by refluxing with precipitated copper in benzene solution on the water-bath for 3 hours. After filtration, the solvent was removed off and the nitrile was distilled, b.p. 100-2°/4 mm., yield 13 g. (Found : N, 7·7. $C_{12}H_{13}O_2N$ requires N, 7.7 per cent).

1-*Methyl*-Δ^2-cyclo*penten-1* : 2-*dicarboxylic Acid* (IV, R=COOH).—The unsaturated nitrile (13 g.) was refluxed with fuming hydrochloric acid (20 c.c.) for 15 hours. The acid was extracted with a large excess of ether, in which, however, it was sparingly soluble. On removal of the solvent, the acid crystallised out in stout needles, m.p. 202°, which rose to 204° after recrystallisation from acetic acid. It is sparingly soluble in water, yield theoretical. (Found : C, 56·8 ; H, 5·7. $C_8H_{10}O_4$ requires, C, 56·48; H, 5·8 per cent).

trans-1-*Methyl*cyclo*pentane-1* : 2-*dicarboxylic Acid* (I).—The unsaturated acid (V, 5 g.) was reduced with 10 times the theoretical quantity of 3% sodium amalgam in a slightly alkaline solution. The filtrate was acidified and thoroughly extracted with ether after saturation with sodium chloride. The oil, obtained after the removal of the solvent, solidified on standing and scratching. On repeated crystallisation from

water, it was obtained in small cubes, m.p. 142°, yield 2 g. (Found : C, 55·9 ; H, 6·9. $C_8H_{12}O_4$ requires C, 55·8 ; H, 6·9 per cent).

β-Ethoxyethyl-acetoacetic Ester (*Ethyl γ-ethoxyacetobutyrate*).—To a well-cooled solution of sodium ethoxide, prepared from sodium (8 g.) and alcohol (92 c.c.), was gradually added a mixture of ethoxyethyl iodide (97 g.) and ethyl acetoacetate (55 g.). The mixture was heated on the water-bath for 12 hours and then diluted with water, extracted with ether and washed with sodium bicarbonate and dried. The ester was obtained as a clear mobile liquid, b.p. 110-13°/7 mm., yield 50 g. (Found : C, 59·9; H, 8·7. $C_{10}H_{18}O_4$ requires C, 59·4 ; H, 8·9 per cent).

γ-Ethoxypropylmethyl Ketone (V).—The above ester (50 g.) was hydrolysed with sulphuric acid (8%, 400 c.c.) by boiling for 20 hours. On cooling, the solution was saturated with ammonium sulphate and extracted with ether. The ethereal extract was dried over calcium chloride and after removal of the solvent through a fractionating column, the ketone was finally obtained from the residue as a mobile liquid, b.p. 169°, yield 20 g. (Found : C, 64·8 ; H, 10·5. $C_7H_{14}O$ requires C, 64·6 ; H, 10·7 per cent).

Ethyl αβ-Dicyano-β-(γ-ethoxypropyl)-butyrate (VI).—The ketone (20 g.), to which a drop of potassium cyanide had been added, was cooled in a freezing mixture. Hydrocyanic acid, generated from potassium cyanide (30 g.) and sulphuric acid (30 c.c. in 45 c.c. of water) was gradually passed into the ketone. After standing overnight at 0°, it was worked up in the usual way, when the cyanohydrin (19 g.) was obtained, b.p. 122°/9 mm. To a mixture of this cyanohydrin (17 g.) and dry alcohol (12 c.c.), cooled in a freezing mixture, was added with shaking, ice-cold alcoholic suspension of ethyl sodiocyanoacetate (prepared from 15 g. of ethyl cyanoacetate and 45 c.c. of alcohol). After standing for 3 days at ordinary temperature, the mixture was decomposed with ice and hydrochloric acid. The heavy oil was extracted with ether, washed with alkali and with water and finally dried. The dicyano-ester was obtained as a viscous liquid, b.p. 170-75°/7 mm., yield 14 g. (Found : N, 10·9. $C_{13}H_{20}O_3N_2$ requires N, 11·1 per cent).

Ethyl α-Cyano-β-(γ-ethoxypropyl)-crotonate.—A mixture of γ-ethoxypropylmethyl ketone (15 g.), ethyl cyanoacetate (11.3 g.), acetamide (2 g.) and glacial acetic acid (24 c.c.) was taken in a flask fitted with a fractionating column and directly heated over a small flame. The temperature was so maintained that acetic acid (24 c.c.) distilled off in about 3-4 hours. The residue was cooled, diluted with water, extracted with ether and washed with sodium bicarbonate. From the ethereal solution the unsaturated ester was isolated, b.p. 135°/5 mm., yield 20 g. (Found : N, 6·3. $C_{12}H_{19}O_3N$ requires N, 6·2 per cent).

Ethyl αβ-Dicyano-β-(γ-ethoxypropyl)-butyrate (VI).—To a solution of the foregoing unsaturated cyano-ester (11 g.) in alcohol (95%, 60 c.c.) was added potassium cyanide (65 g. in 35 c.c. of water). The mixture became warm and was cooled in ice. Next water (35 c.c.), and hydrochloric acid (d 1·15, 8 c.c.) were added with cooling. After standing for 20 minutes at ordinary temperature the reaction mixture was poured into 250 c.c. of ice-cold dilute hydrochloric acid. The precipitated heavy oil was extracted with ether, dried and distilled, yield 10·5 g., b.p. 167-69°/6 mm. (Found : N, 11·6. $C_{13}H_{20}O_3N$ requires N, 11·1 per cent).

Ethyl α-Methyl-α-(-γ-ethoxypropyl)-succinate.—The above dicyano-ester (45 g.) was hydrolysed with dilute sulphuric acid (108 c.c. in 360 c.c. of water) for 72 hours, when most of the oil went into solution. After saturation with ammonium sulphate, the solution was thoroughly extracted with ether. The reddish gum (30 g.), obtained from ether, was dried in vacuum and esterified by refluxing for 24 hours with a mixture of alcohol (200 c.c.) and sulphuric acid (30 c.c., d 1·84). After working up in the usual way, it was collected at 134°/5 mm., yield 26 g (Found : C, 61·3 ; H, 9·05. $C_{14}H_{26}O_5$ requires C, 61·3 ; H, 9·4 per cent).

It may be mentioned that the use of sulphuric acid of higher concentration for hydrolysis resulted in the decomposition of the product.

Ethyl αδ-Dibromovalerate (VII, R=H).—Ethyl γ-bromopropylmalonate (26 g.) was hydrolysed with hydrobromic acid (48%, 100 c.c.) for 8 hours. After dilution with water, the heavy layer was extracted with ether and the extract dried in vacuum for several days after removal of the solvent. It was subsequently treated with thionyl chloride (8 c.c.) and then heated on the water-bath for about 2 hours until the initial reaction was over. After cooling, bromine (8 c.c.) was gradually added to the mixture and it was left overnight at ordinary temperature ; after which it was heated for a day with additions of bromine until the colour persisted. The mixture was then treated with alcohol (50 c.c.) and refluxed for 2 hours. After working up in the usual way, it was collected at 111-12°/5 mm., yield 19 g. (Found : Br, 55·1. $C_7H_{12}O_2Br_2$ requires Br, 55·5 per cent).

Ethyl 1-Cyano-cyclopentane-1 : 2-dicarboxylate (VIII).—The foregoing dibromo-ester (19 g.), diluted with a little alcohol, was added slowly to a well-cooled suspension of ethyl sodiocyanoacetate in alcohol, prepared from cyanoacetic ester (15 g., 2 mols), 3·3. g. of sodium (2 mols) and alcohol (50 c.c.). Considerable amount of heat was evolved and the alcohol began to boil. After standing at ordinary temperature overnight, the mixture was refluxed over a free flame for 24 hours. The product was poured into water, extracted with ether and the extract was thoroughly washed with water, when most of the colour was removed. The residue was worked

up in the usual way and then distilled in vacuum, the fraction b.p. 130-42°/4 mm. being collected, yield 11·5 g. On redistillation practically the whole of it passed over at 132°/3 mm. as a colourless viscous oil (Fuson, *loc. cit.*, records b p. 135-36°/3·5 mm for this compound). (Found : C, 60·1 ; H, 6·8. Calc. for $C_{12}H_{17}O_4N$: C, 60·2 ; H, 6·7 per cent).

The above cyano-ester was hydrolysed according to Fuson (*loc. cit.*), when a substance, m. p. 153-58°, evidently crude *cyclo*pentane-1: 2-dicar boxylic acid, was isolated. This was converted into the anhydride of the *cis*-form by refluxing with acetic anhydride for 7 hours, whereby it was obtained as a gelatinous mass boiling at 100°/4 mm. This, on boiling with water gave the pure *cis*-acid, m. p 141°.

Ethyl α-Methyl-α-carbethoxy-δ-bromovalerate.—To ethyl sodiomethyl-malonate, prepared in benzene solution by the gradual addition of ethyl methylmalonate (50 g.) to finely powdered sodium (6 g.), trimethylene bromide (60 g.) was added and the mixture refluxed on the water-bath for 16 hours. After working up in the usual way, the fraction boiling at 150-75°/14 mm. was collected and redistilled at 153-55°/12 mm., yield 28 g. (Found : Br. 27·0. $C_{11}H_{19}O_4Br$ requires Br, 27·1 per cent).

Ethyl αδ-Dibromo-α-methylvalerate (VII, R=Me).—The above ester (25 g.) was hydrolysed with hydrobromic acid (48%, 150 c.c.) by refluxing over a free flame for 16 hours. On the addition of water, a heavy oil separated at the bottom, which was extracted with ether. After removal of the solvent, the residual liquid was dried over potassium hydroxide for 2 days, yield 12 g. This product (18 g.) was treated with phosphorus pentabromide and the mixture allowed to stand for 4 hours at the ordinary temperature Bromine (8 c. c.) was added and the mixture left overnight. It was heated on the water-bath for 12 hours with the addition of a further quantity of bromine until the colour persisted. Then it was poured into absolute alcohol (125 c.c.) with ice-cooling. After refluxing for 2 hours it was worked up in the usual way, b. p. 118-20°/6·5 mm., yield 24 g (Found : Br, 50·0 $C_8H_{14}O_2Br_2$ requires, Br, 50·3 per cent).

Ethyl 1-*Cyano-2-methyl*-cyclo*pentane-1*: 2-*dicarboxylate* (IX).—The above dibromo compound (23 g) was added to ethyl sodiocyanacetate, prepared from ethyl cyanacetate (17 g.), sodium (3·6 g.) and alcohol (55 c.c.), when the initial vigour of the reaction subsided, it was refluxed over a free flame for 30 hours. The product was worked up as before and the fraction, b. p. 110-22°/1 mm., collected and redistilled at 118-20°/1 mm., yield 15·5 g. (Found : C, 61·3; H, 7·5 $C_{13}H_{19}O_4N$ requires C, 61.6; H, 7·5 per cent).

trans-1-*Methyl*cyclo*pentane-1*: 2-*dicarboxylic Acid* (I).—The above cyano-ester (6 g.) was hydrolysed with fuming hydrochloric acid (35 c.c.)

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over a free flame for 30 hours, then concentrated and cooled when crystalline precipitate separated. The crude acid had m. p. 137-39°. On crystallising from water, it was obtained in beautiful radiating cubes, m. p. 143°, the mixed m. p. with the acid obtained previously showed no depression. (Found : C, 55·9 ; H, 6·8 $C_8H_{12}O_4$ requires C, 55·8 ; H, 6·9 per cent).

cis-1-*Methylcyclopentane*-1 : 2-*dicarboxylic Acid* (I).—8 G. of the above cyano-ester (X) was heated in a sealed tube with fuming hydrochloric acid (35 c.c.) for 3 hours at 160° and at 180° for 9 hours The mixture (slight tar formed) was extracted with ether and the residue from ether was repeatedly charcoaled in aqueous solution. Some difficulty was experienced in crystallisation, for it evidently consisted of a mixture of *cis-* and *trans*-forms. Ultimately the solution was very slowly cooled after the addition of a few drops of hydrochloric acid and the separated mixture had m.p. 107-128°. (Found: C, 56·08; H, 6·56. $C_8H_{12}O_4$ requires C, 55·8, H, 6·9 per cent).

The mixture (2 g.) was refluxed with acetic anhydride (20 c.c.) for 10 hours and after removal of the latter, the anhydride was obtained as a gelatinous mass showing a tendency to crystallisation and b p. 101°/4 mm., yield 1.1 g. A residue also remained in the flask. The anhydride was refluxed with dilute hydrochloric acid for 7 hours. On concentrating the solution, a sandy crystalline powder separated. This was recrystallised from water containing hydrochloric acid, when it was obtained as clusters of small cubes. A fresh sample dried over a porous plate showed m. p 124-26° with previous softening at 120°, but after drying in *vacuo* over sulphuric acid for a week had m. p. 120-25°. (Found: C, 56·3 ; H, 6·4 $C_8H_{12}O_4$ requires C, 55·8 ; H, 6·9 per cent).

Conversion of the trans-*Acid into* cis- *form and vice versa.*—The pure acid (10 g., m. p. 142°) was heated with fuming hydrochloric acid (15 c.c) at 190-200° for 12 hours. The separated solid was collected with adhering tarry matter and repeatedly treated with animal charcoal in aqueous solution until colourless. The solution was allowed to crystallise slowly after the addition of a little hydrochloric acid. The m. p. of successive crops was indefinite between 120 and 135° showing thereby that the *trans*-acid was contaminated with the *cis*-isomer. Similarly when 3 g. of the *cis*-acid were treated under similar conditions, the product was found to melt within 5° of the value recorded for that of the pure *cis*-acid (124-26°)

My grateful thanks are due to Prof. P. C. Mitter for his valuable suggestions, kind interest and encouragement during the course of this investigation.

SYNTHESIS OF NEW LOCAL ANAESTHETICS. PART V.

BY K. N. GAIND, J. N. RAY AND BADRI SARIN.

Diethylamino and piperidino derivatives of 5-, 6- and 8-acylaminoquinolines have been prepared and their local anaesthetic properties studied. Similar compounds of 2-aminocarbazole have also been synthesised and are found to have potent anaesthetic efficiency as tested on rabbit's cornea.

In order to find out whether a simple amide grouping can act as an anchor for the production of local anaesthetic properties, some amides with a basic side-chain have been described (Part IV). It seemed that the extension of the principle to the quinoline series will result in the production of compounds of even more potent local anaesthetic activity. For this purpose, 6-aminoquinoline has been converted into chloroacyl derivatives (I) and these have been further interacted with diethylamine and piperidine

$$NH \cdot CO \cdot (CH_2)_n Cl \qquad (I) \qquad NH \cdot CO \cdot (CH_2)_n R \qquad (II)$$

The related products (piperidino-or diethylamino-acylaminoquinolines) with the side-chain at position 5 and 8, have also been prepared. The latter (side-chain at 8) have been found to have pronounced local anaesthetic activity, whilst the activity is much less in those compounds where the side-chain is attached at position 5 or 6.

The dihydrochloride of 3-ω-piperidinoacetylaminocarbazole (III) has been found to have very strong local anaesthetic properties.

$$NH \cdot CO \cdot (CH_2)_n \cdot N (C_5H_{10}) \qquad (III)$$

NH

EXPERIMENTAL.

6-Aminoquinoline was prepared essentially by the method of Knueppel (*Annalen*, 1900, **310**, 75), but the dark viscous product was extracted in a Soxhlet with ether and then recrystallised from benzene, m.p. 115°, yield 7 g. from 15 g. of 6-nitroquinoline.

6-ω-*Chloroacetylaminoquinoline* (I, n=1).—The foregoing aminoquinoline (5 g.) in benzene (30 c.c.) suspension was shaken with normal sodium carbonate solution in such a manner that the base accumulated at the

interface. Chloroacetyl chloride (1 mol.), dissolved in benzene, was made to run along the sides of the flask which was kept rotated. After standing for 2 hours, the mixture was thoroughly shaken, the solids collected and then crystallised from hot toluene in prisms, m.p. 154°, yield 4·5 g. (Found : N, 13·30. $C_{11}H_9ON_2Cl$ requires N, 13·15 per cent). Alternatively the aminoquinoline (5 g.), dissolved in acetic acid (20 c c.) and a saturated solution of sodium acetate in water (20 c.c.), was treated with chloroacetyl chloride (2·7 c.c.) in the ice-cold. The product was precipitated with a large quantity of water and crystallised from hot toluene, yield 5 g.

6-ω-*Piperidinoacetylaminoquinoline* (II, $n=1$, R replaced by piperidino.).—The foregoing chloro compound (4·5 g.), dissolved in absolute alcohol (100 c.c.), was mixed with anhydrous sodium carbonate (1·6 g) and then refluxed after the addition of piperidine (2·5 g.) for 5 hours. The residue after the removal of alcohol from the filtered solution was well washed with water, dissolved in ether, dried, and then the solvent removed. Crystallised from hot petroleum ether (pointed rods), it had m.p. 101°, yield 4 g. (Found : N, 15·61. $C_{16}H_{19}ON_3$ requires N, 15·40 per cent). The hydrochloride, prepared with ethereal hydrogen chloride in ether, crystallised from a mixture of alcohol and ether, m.p. 133°. (Found : Cl, 20·60. $C_{16}H_{19}ON_3$, 2HCl requires Cl, 20·76 per cent).

Similarly 6-ω-*diethylaminoacetylaminoquinoline* was prepared with diethylamine in place of piperidine and was crystallised from petroleum ether in rectangular plates, m.p. 86°, yield 3 g. (Found : N, 16·25. $C_{15}H_{19}ON_3$ requires N, 16·34 per cent). The hydrochloride crystallised from a mixture of alcohol and ether, m.p. 250°. (Found : Cl, 21·80. $C_{15}H_{19}ON_3$, 2HCl requires Cl, 21·4 per cent).

6-β-*Chloropropionylaminoquinoline* was prepared in a manner analogous to the related chloroacetyl derivative and the product crystallised from dilute alcohol in prisms, m.p. 178°. (Found : N, 11·98. $C_{12}H_{11}ON_2Cl$ requires N, 11·84 per cent).

6-β-*Piperidinopropionylaminoquinoline*, prepared from the foregoing chloro compound in the manner described, was crystallised from dilute alcohol in pentagonal plates, m.p. 67°. (Found : N, 14·86. $C_{17}H_{21}ON_3$ requires N, 15·17 per cent).

6-ω-*Diethylaminopropionylaminoquinoline*, prepared as described before, was obtained as an oil. The base was converted into the dipicrate, m.p. 180° after crystallisation from alcohol. (Found : N, 17·2. $C_{28}H_{27}O_{13}N_9$ requires N, 17·28 per cent).

The analogues of the foregoing compounds were prepared from 8- and 5-aminoquinolines by method essentially the same as described and the compounds are described in Table I.

TABLE I.

Substance.	Crystallised from.	M.p.	Analysis. Found.	Calc.
8-ω Chloroacetylamino-quinoline	33% Alcohol	131°	N, 12.56%	N, 12.72%
8-ω Piperidinoacetylamino-quinoline hydrochloride	Dilute acetone.	77° (decomp.)	11·83	12·28
8-β-Chloropropionylamino-quinoline	Dilute alcohol	88°	11·76	11·94
8-β-Piperidinopropionyl-aminoquinoline	Petroleum ether	108°	14·37	14·84
The *hydrochloride.*	Alcohol-ether	189° (decomp.)	11·79	12·01
8-β Diethylaminopropionyl-aminoquinoline dipicrate	Alcohol	167°	17·52	17·28
5-ω-Chloroacetylamino-quinoline hydrochloride (prepared in ethereal solution of the reactants)	Alcohol	157°	Cl, 27·48	Cl 27·62
5-ω-Piperidinoacetyl-aminoquinoline.	Water	62°	N, 15·86	N, 15·61
5-ω-Diethylaminoacetyl-aminoquinoline dipicrate	Alcohol	203°	17·48	17·63
5-β-Chloropropionylamino-quinoline hydrochloride (prepared in ether solution of reactants)	Alcohol	226° (decomp.)	·10·13	10·33
Dipicrate of 5-β piperidino-propionylamino-quinoline.	Alcohol	230°	16·81	17·00

Carbazole Series.

Substance.	Crystallised from.	M.p.	Analysis. Found.	Calc.
3-ω-Chloroacetylamino-carbazole	Dilute alcohol	203°	N, 10.78	N, 10.85
(a) 3-ω Piperidinoacetyl-aminocarbazole.	Dilute alcohol	175°	13·52	13.63
Dihydrochloride of (a)	Alcohol-ether.	280°	Cl, 18·34	Cl, 18.08
(b) 3-ω-Diethylaminoacetyl-aminocarbazole	Dilute alcohol	99°	N, 14.51	N, 14.21
Dihydrochloride of (b)	Alcohol-ether.	232°	Cl, 19.02	Cl, 19.58
3-β-Chloropropionylamino-carbazole.	Alcohol	228° (decomp.)	N, 10.42	N, 10.20
(c) 3-β-Piperidinopropionyl-aminocarbazole	Benzene	219°	N, 14.86	N, 15 57
Dihydrochloride of (c)	Alcohol-ether.	298°	Cl, 17.78	Cl, 18 c2

3-Aminocarbazole was prepared according to Perkin and Plant *(J. Chem. Soc.,* 1924, **125,** 1512).

The above substances were tested for local anaesthetic activity by the rabbit's cornea method and Table II shows the results.

TABLE II..

(The figures in parenthesis are for cocaine used as a standard).

	Time for onset of anaes- thesia : complete loss of reflex action.	Duration for which complete loss of reflex action lasted.
Hydrochloride of 6-ω-piperi- dinoacetylaminoquinoline	Never complete (1-1/2 min)	Incomplete anaesthesia for 28 min. (36 min.)
Hydrochloride of 6-ω-diethyl- aminoacetylquinoline	,, (1 min)	Incomplete anaesthesia for 24 min. (37 min.)
Hydrochloride of 6-β-piperi- dinopropionlyamino quinoline	,, (1 min)	,, for 12 min. (36 min.)
Hydrochloride of 6-β-diethyl- aminopropionylamino- quinoline.	,, (1-1/2 min)	,, for 10 min (36 min)
Hydrochloride of 8-ω-piperidi- noacetylaminoquinoline	4 minutes (1 min.)	48 min. (35 min.)
Hydrochloride of 8-β-piperi- dinopropionylamino- quinoline	3 minutes (1 min.)	45 min. (36 min.).
Hydrochloride of 8-β-diethyl- aminopropionylamino- quinoline	4 minutes (1 min.)	44 min. (37 min)
Hydrochloride of 5-ω- piperi- dinoacetylaminoquinoline	Never complete (1 min.)	Incomplete lasting for 26 min (36 min.)
Hydrochloride of 5-ω-diethyl- aminoacetylaminoquinoline	Never complete (1 min.)	,, for 24 min. (36 min)
Hydrochloride 5-β-piperi- dinopropionylamino- quinoline	Never complete (1 min.)	Incomplete lasting for 23 min. (35 min.)
Hydrochloride of β-diethyl- aminopropionylamino- quinoline	Never complete (1 min.)	Incomplete lasting for 18 min (36 min.)
Hydrochloride of 3-ω-piperi- dinoacetylaminocarbazole	2 min. (1-1/2 min.)	94 min. (37 min.)
Hydrochloride of 3-ω-diethyl- aminoacetylamino- carbazole	2-1/2 min. (1 min.)	86 min. (36 min.)

From the foregoing table it will appear that only 8-aminoquinoline derivatives possess local anaesthetic activity, whilst the related 5 or 6-amino quinolines do not show satisfactory results. The derivatives of 3-amino-carbazole cause profound local anaesthesia, approximetely possessing about three times the potency of cocaine.

The toxicity and other details are being worked out   One of us (K. N. G) is indebted to the Lady Tata Memorial Trust for a maintenance grant.

COMPLEX CHROMIUM SELENATES.

By Prodosh Chandra Raychoudhury

Two modifications of chromium selenate, blue and green, have been described and their properties studied. They differ from the compounds described by Meyer.

Three different modifications of chromium sulphate are described one of which is violet and the other two green. The green chromic sulphates, from a consideration of their properties, are regarded to have complex constitutions. One of these, in which all the sulphate radicals are non-ionisable, is considered to be chromium-chromisulphate, $Cr[Cr(SO_4)_3]$. Many complex compounds of chromium sulphate, such as chromo-sulphates, chromo-sulpho-chromates and the corresponding acids have been described by Re-coura (*Compt. rend.*, 1892, **114**, 477; 1893, **116**, 1367; 1893, **117**, 37, 101; *Bull. Soc. chim.*, 1896, iii, **15**, 315; 1897, iii, **17**, 934).

In a previous paper (*J. Indian Chem. Soc.*, 1939, **16**, 653) it has been shown that chromic chromate also possesses a complex constitution, $Cr'''[Cr'''(CrO_4)_3] 3H_2O$ or $Cr'''[Cr'''(CrO_4)_3. (H_2O)_3]$

It is well known that sulphuric and selenic acids resemble each other closely and it was not unexpected that complex compounds of chromium and selenic acid analogous to complex chromium sulphate would be reported. Meyer (*Z. anorg. allg. Chem*, 1921, **118**, 1) has described two modifications of complex chromium selenates, green and violet, besides a triselenatochromic acid. Sarkar and Bhattacharyya have studied the properties of chromoselenic acid and chromosulphoselenic acid and their salts (*J. Indian Chem. Soc.*, 1930, **7**, 765).

The violet and green selenates of Meyer were represented by the following constitution and formulae respectively. $[Cr(H_2O)_6]_2(SeO_4)_3$. 3 or $4H_2O$ prepared from violet chromium nitrate and concentrated selenic acid, and $[Cr(SeO_4)(H_2O)_5]_2SeO_4$ or $[\{Cr(H_2O)_6\}_2SeO_4](SeO_4)_2$ prepared from the violet salt by drying it at 90°.

In the present paper two modifications of chromium selenate, blue and green, have been described, which differ in composition and in certain properties from those described by Meyer.

EXPERIMENTAL.

Blue Chromium Selenate, $Cr_2 (SeO_4)_3$, $17H_2O$.

A large excess of freshly prepared silver selenate was triturated with

a conccentrated solution of chromium chloride. The mixture was kept aside for two days and then filtered. The blue filtrate was tested for silver and chlorine and any excess of either was removed by the cautious addition of chromium chloride or silver selenate. Any precipitate formed was removed by filtration. The blue solution was afterwards evaporated in a vacuum desiccator to dryness. The residue was digested with glacial acetic acid, filtered and kept in a desiccator over KOH till free from acetic acid. [Found: Cr, 12·46; Se, 28·39. $Cr_2(SeO_4)_3$, $17H_2O$ requires Cr, 12·40.; Se, 28·27 per cent]. The substance forms a blue powder which loses 8 molecules of water at 105°, and 13·5 molecules at 165°.

Cryoscopic measurements.

Substance (g./100 c.c. water).	Dep. Δ.	Mol. wt. m.	Vant-Hoff's factor $i=\dfrac{m}{M}$.	Degree of dissociation. $a=\dfrac{i-1}{n-1}$.
1·590	0·146	196	2·719	0·43 approx.
0·795	0·088	162·6	3·278	0·57

(M = mol. wt. calculated on anhydrous basis = 533)

Molecular conductivity at 35°.

v (dilution in litres) ...	128	256	512	1024	2048	4096
μ_v	411·39	476·93	542·21	621·21	718·85	814·56

The conductivity values correspond with those found for the violet chromium sulphate solution at the same temperature by Winston and Jones (*Amer Chem. J.*, 1911, **46**, 368).

v (dilution in litres) ...	128	512	1024	4096
μ_v	360·5	502	598	859

The *magnetic susceptibility* of the blue salt at 30° measured in a Curie's balance gave $\chi_m = 12\cdot8 \times 10^{-6}$ and $p_{weiss} = 18\cdot0$.

The values are in good agreement with that for simple chromic ion.

The substance is very soluble in water. The solution of the blue salt becomes green on heating.

A freshly prepared blue solution treated with an excess of a solution of barium nitrate gives a white precipitate of barium selenate in the cold. The filtrate on boiling gives a further white precipitate of barium selenate. On treatment with dilute silver nitrate the solution of the blue salt gives a white precipitate after sometime. The solution reacts acid to litmus. Tl is blue salt' differs from the violet chromic selenate, described by Meyer, having the constitution $Cr_2(SeO_4)_3$, 15 or $16H_2O$, in which the whole of the selenate is completely and immediately precipitated by salts of barium. Moreover, the blue salt unlike Meyer's violet selenate gives no green precipitate of triselenato-chromic acid, $H_3[Cr(SeO_4)_3]$, when its boiling solution is treated with alcohol.

Green Chromium Selenate, $Cr_2(SeO_4)_3$, 13 H_2O.

The blue solution of $Cr_2(SeO_4)_3$, 17 H_2O was evaporated to dryness on a water-bath. The green residue obtained was digested with glacial acetic acid and dried over solid KOH in a desiccator till tree from acetic acid. [Found : Cr, 13·43; Se, 30·60. $Cr_2(SeO_4)_3$, $13H_2O$ requires Cr, 13·55 ; Se, 30·94 per cent] The substance forms a beautiful green powder which loses 3·5 molecules of water at 105° and 6 molecules at 165°.

Cryoscopic measurements.

Substance (g./100 c.c. water)	Dep. Δ	Mol wt. m	Vant Hoff's factor $i = \dfrac{m}{M}$.	Degree of dissociation. $\alpha = \dfrac{i-1}{n-1}$.
1·5015	0·185	146·2	3·645	0·661
0·7505	0·106	127·6	4·186	0 796

($M.$ = Mol. wt. calculated on anhydrous basis = 533).

Molecular conductivity at 35°.

$v.$ (dilution in litres)...	64	128	256	512	1024	2048	4096
μ_v	422·21	481·02	546·56	611·84	691·2	759·8	847·8

The *magnetic susceptibility* of the green salt at 30° measured in a Curie's balance gave $\chi_m = 12·46 \times 10^{-6}$ and $p_{weiss} = 17·0$ approx.

The green salt is soluble in water with great difficulty to a green solution which reacts acid to litmus.* The green solution on treatment with excess of barium nitrate gives a white precipitate of a barium selenate in the cold. The filtrate on boiling gives a further quantity of barium selenate Silver nitrate solution gives a small quantity of silver selenate. The blue salt is easily convertible into the green variety with rise of tempera-ture.

From a consideration of their properties it seems that there is a little difference in the behaviour of the two salts. The blue salt possibly contains less of selenate radical, co-ordinately bound, than the green variety. The green selenate described in this paper possibly corresponds with that described by Meyer differing only in the amount of hydration. The blue salt may be regarded as the intermediate product between Meyers' violet and green selenates as represented below :

$$[Cr(H_2O)_6]_2(SeO_4)_3 \rightarrow [Cr(H_2O)_5\text{---}SeO_4\text{---}Cr(H_2O)_5](SeO_4)$$

Violet   Blue

$$\rightarrow [Cr{(H_2O)_5 \atop (SeO_4)}]_2 SeO_4.$$

Green

My sincerest thanks are due to Prof. P. Rây, who suggested this piece of work, for his kind guidance and advice during the course of work in his laboratory.

THE INFLUENCE OF TEMPERATURE ON THE ELECTRICAL CONDUCTIVITY AND VISCOSITY OF AQUEOUS MERCURIC CHLORIDE.

By Sridhar Sarvottam Joshi and Dushyant Narasingasa Solanki.

Conductivities and viscosities of aqueous mercuric chloride of $0.125M - 0.00939M$ cor c. have been determined within $15°$ to $40°$. The conductivity is extremely low almost equal to that of non-electrolyte It increases, however, more rapidly with temperature (about 3.8 to 6.2%) than is observed in aqueous solution of strong electrolytes. It is considered that the ionisation of $HgCl_2$ involves, besides those derived from its binary dissociation, other and more complex ions. This might explain in part the observed discrepancy from Kraus and Bray's formula. Authors' data for the influence of temperature on conductivity are in agreement with Kohlrausch's equation. The variation of viscosity with concentration and temperature can adequately be expressed by Berl and Umstätter and Karrer's equations The temperature coefficients of viscosity of $HgCl_2$ solutions are almost equal to those of the pure solvent, water. It is also seen that the temperature coefficient of viscosity of solvent (water) remains unaltered inspite of the varying concentration of $HgCl_2$ present in the system. Authors' data for the influence of temperature on viscosity are in agreement with Bousfield and Lowry's equation.

The very low conducting nature of mercuric chloride, both in the solid and molten state was, perhaps, first established by Faraday (*Phil. Trans.*, 1834, **124**, 77; 1838, **128**, 83), Clark (*Phil. Mag.*, 1885, *v*, **20**, 37), Hampe (*Chem. Ztg.*, 1887, **11**, 904), Fritsch (*Ann. phys. chim.*, 1897, *ii*, **60**, 308), Foot and Martin (*Amer. Chem. J.*, 1909, **41**, 454) and others. Cold saturated solution of mercuric chloride was found by Hampe (*loc. cit.*), Faraday (*loc. cit.*) and Morse (*Z. physikal. Chem.*, 1902, **41**, 709) to be a poor conductor of electricity. The conductivity of aqueous solutions has been measured by Grotrian (*Wied. Ann.*, 1883, **18**, 192), Fitzpatrick (*Phil. Mag.*, 1887, *v*, **24**, 384), Ley and Kissel (*Ber.*, 1899, **32**, 1358), Jones and Oata (*Amer. Chem. J.*, 1899, **22**, 12), Kahlenberg (*J. Phys. Chem.*, 1901, **5**, 339) and Holdermann (*Arch. Pharm.*, 1905, **243**, 616). Ley (*Ber.*, 1897, **30**, 2195; *Z. physikal. Chem.*, 1899, **30**, 247) demonstrated that the conductivities are rather less with plain than with platinised platinum electrodes. Arctowsky (*Z. anorg. Chem.*, 1885, **9**, 188) found that the electrical conductivity of aqueous solution increases

perceptibly on standing, presumably because of hydrolysis and the corresponding formation of hydrochloric acid. That the dissociation constant for $HgCl_2$ is of a very low order and that the dissociation takes place in stages has been demonstrated by the work of Luther (*Z. physikal. Chem.*, 1901 36, 402; 1904, 47 107) and Sherill (*ibid.*, 1903, 43, 734; 1904, 47, 103). Kohlrausch and Nippoldt (*Ann. phys. chim.*, ii, 26, 161) and Kohlrausch and Grotrian (*Dingl. Polyt. J.*, 114, 337) carried out investigations on the temperature coefficients of conductivity of several electrolytes in aqueous solutions. Their results were further confirmed by Schaller (*Z. physikal. Chem.*, 1898, 25, 497). Eversheim (*Ann. Physik*, 1902, iv, 8, 539) studied the electrical conductivity of $HgCl_2$ in organic solvents, ethyl chloride and ethyl ether, at different temperatures and also measured the dielectric constant at different temperatures. Rasch and Hinrichsen (*Z Elektrochem.*, 1908, 14, 41) from conductivity measurements at different temperatures arrived at the expression

$$\frac{d \log K}{dT} = -\frac{q}{RT^2},$$

connecting K, the conductivity of an electrolyte and temperature. Noyes (*J Amer. Chem. Soc.*, 1908, 30, 335) from the study of the effect of temperature on the conductivity and ionisation of acids, bases and salts came to a definite conclusion that in general the ionisation decreases steadily with rise of temperature in the case of every substance investigated by the authors; the effect of temperature on ionisation of salts is comparable with its effects on the dielectric constant of water. Bousfield and Lowry (*Proc. Roy. Soc.*, 1902, A71, 42) concluded that the two factors which determine the form of temperature-conductivity curves are : (a) the increase of η and decrease of ionic mobilities with falling temperature ; (b) the decrease of ionisation with rising temperature; and the temperature coefficient of conductivity will be positive or negative according as one or the other of these two factors predominates. The authors also showed that the viscosity-temperature relation can be expressed by the formula

$$\eta_{18} = \eta_t \left[1 + a(t-18) + \beta(t-18)^2\right]$$

analogous to Kohlrausch's formula (*Proc. Roy. Soc.*, 1903, A71, 338) for conductivity,

$$K_t = K_{18}\left[1 + a(t-18) + \beta(t-18)^2\right]$$

the coefficients α, and β, being nearly the same in both the formulae when applied to water. Jones and West (*Amer. Chem. J.*, 1905, **34**, 357; 1909, **42**, 520) showed that the percentage dissociation and percentage temperature coefficients of conductivity decrease as the temperature is raised. Their results are in close harmony with the observations of Ramsay and Shields (*J. Chem. Soc.*, 1893, **63**, 1089) and Dutoit and Astons hypothesis. The data of Vonwiller (*Phil. Mag.*, 1904, *vi*, **7**, 655) also lead to the same conclusions. Jones (*Amer. Chem. J.*, 1906, **35**, 445) further pointed out the bearing of hydrates on temporary coefficients of conductivity in aqueous solutions. The relation between the nature and properties of solvent and its ionising capacity, electrical conductivity and its temperature coefficients in aqueous and non-aqueous solutions of salts have been investigated by many workers*.

From the viscosity measurements of a large number of electrolytes Taylor and Moore (*Proc. Roy. Soc. Edin.*, 1908, **27**, 461), Getman (*J. Amer. Chem. Soc.*, 1908, **30**, 721; *J. chim. phys.*, 1907, **5**, 344) and others have shown that there are two types of salts, one type showing 'positive' viscosity effect and the other type showing 'negative' viscosity effect and that the viscosity of salt solutions cannot be regarded as simply an additive property. They further showed that the cations in opposition to undissociated molecules and anions, tended to diminish the viscosity of water and in general, this lowering effect of the cation was shown to be proportional to its atomic volume by Jones and Veazey (*Amer. Chem. J.*, 1907, **37**, 405); anions and non-dissociated molecules, on the other hand, were shown to increase the viscosity of the solvent. The molecular complex formation also was shown to affect the viscosity to a remarkable extent. Tamman and Rabe (*Z. anorg. Chem.*, 1927, **162**, 17) studied the effect of temperature on the surface tension of electrolytic solutions. A general formula of the type

$$\eta_{H_2O}/\eta = 1 - 0.02013\sqrt{C} - 0.20087\,C$$

has been deduced by Jones and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 2950), the coefficient $\sqrt{C}$ is negative for strong electrolytes and zero for non-electrolytes and the coefficient C is negative for those salts which increase the viscosity of water at all concentrations. Falkenhagen and

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* Giulio Coffetti (*Gazzetta*, 1903, **33**, 53), White and Jones (*Amer. Chem. J.*, 1909, **42**, 520), Inclan (*Annal. Fis. Quim.*, 1906, **4**, 94), Kohlrausch and Maltby (*Wiss. Abhandl. Phys. Tec. Reich-Sanstalt*, 1900, **3**, 155) and others.

Dole (*Z. physikal. Chem.*, 1929, **B6**, 159) proposed a square root law for the viscosity of strong electrolytes, $\eta_c = \eta_o (1 + A \sqrt{C})$ where C is the normality of the solution, η_c and η_o, the viscosity coefficients of the solution and solvent respectively, and A is a constant. Berl and Umstätter and Karrer (*Z. physikal. Chem.*, 1931, **152**, 284) proposed equations, to express the variation of viscosity with temperature and concentration,

$$\log \eta = \frac{B}{T} - A, \quad \log \eta = KC,$$

where C is volume concentration, T, the absolute temperature K, A, and B are constants. The present work on aqueous $HgCl_2$ was suggested by observation of its high coagulative power (in contrast with low ionisation and conductivity) and other anomalous behaviour as a coagulant (*cf.*, Joshi and Kulkarni, *J. Indian Chem. Soc.*, 1936, **13**, 439 ; Joshi and Menon, *ibid.*, 1937, **14**, 103 ; Joshi and Ram Das, *ibid.*, 1937, **14**, 167). Joshi and Krishna Rao (results to be published] have found that $HgCl_2$ has an abnormally high adsorbability towards animal charcoal and colloid $As_2 S_3$. Similar deviations from normality as revealed by conductivity measurements were also noticed in its behaviour towards aqueous benzoic acid (Joshi and Solanki, *J. Indian Chem. Soc.*, 1937, **14**, 323). The very considerable amount of data on the conductance of a large number of substances obtained by Kohlrausch (*loc. cit.*), Melcher and Cooper (*loc. cit.*), Bousefield and Lowry (*loc. cit.*), and Jones (*loc. cit.*) has served to show their marked utility together with those for the viscosity of the medium at different temperatures, in the classification of the solutes in respect of their molecular and ionising behaviour. It was of interest therefore, to study the behaviour of $HgCl_2$ in the light of the above theories.

EXPERIMENTAL.

Conductivity determinations of aqueous mercuric chloride (Merck's guaranteed extra pure) were made at 15°, 20°, 25°, 30°, 35°, and 40°. The containers were all of high resistance Jena glass. The conductivity cell used was of pyrex glass with the platinum electrodes, each of 1 sq. cm. area, fixed vertically, the inter-electrode distance being 1 2 cm. The bridge employed for the determination of electrolytic resistances was Pye's modified Post Office Box of dial resistance type ; a small Kohlrausch coil

was used as an A. C. generator. The conductivity water used for experiments was prepared by distilling twice distilled water in Hartley's conductivity still and collecting only the middle fraction, the first and the last fractions being rejected. This stock of water which was used for making the various solutions was tested for its constancy of conductivity. The cell constant was determined every now and then by using freshly prepared $N/50$-KCl solution at $25 \pm 0 \cdot 05°$. The same cell constant was used for calculating the conductivity at the remaining temperatures, ranging from $15°$ to $40°$, the variation of the cell constant with temperature especially for $10°$ to $15°$ differences being negligible. The electrodes with freshly platinised surfaces were always kept immersed in conductivity water after the completion of an experiment.

Fresh solution of $HgCl_2$ was prepared at every temperature; dilution was made to the exact mark at the respective temperature to avoid the volume changes due to changes in densities. Throughout the experimental procedure the method of successive dilution was adopted, the observations being recorded in the order of their determination i.e., from concentrated to dilute solutions.

The viscosity determinations of these solutions were also made at different temperatures $15°$, $20°$, $25°$, $30°$, $35°$, and $40°$ by adopting Scarpa's method (*Gazzetta*, 1910, **40**, 271) modified by Farrow (*J. Chem. Soc.*, 1912 **101**, 347) and later on further modified by Joshi and Nanjappa (*J. Indian Chem. Soc.*, 1934, **11**, 133 et seq.). Extreme precautions were taken specially in cleaning the viscometer and in maintaining the temperature control within $0 \cdot 05°$.

In Tables I to IV are recorded the values for the conductivities of mercuric chloride.

Tables VII to X record the values for the temperature coefficients of conductivity for different concentrations and for different temperature ranges.

Table XI gives in absolute units the viscosities at different temperatures together with their logarithms.

In Tables XII-XV are recorded the values for the temperature coefficients of viscosity for different concentrations and for different temperature ranges.

In the following tables C stands for concentration in moles per litre, R for resistance in ohms, κ for specific conductivity in mhos, η for viscosity of solution, η_0 for viscosity of water and Λ for molecular conductivity corrected for viscosity in mhos.

TABLE I.

Conductivity of $HgCl_2$ *solutions.*

Temp. $= 15° \pm 0.05°$. Cell constant $= 0.3776$. Sp. conductivity of water $= 1.035 \times 10^{-6}$ mhos.

C.	R.	κ.	η/η_0.	Λ.	$C\Lambda$.	$1/\Lambda$.	Log $(C\Lambda)$.	Log $[C\Lambda^2]$
0·125	4267	0·00008744	1·018	0·7124	0·08904	1·404	$\bar{2}$·9496	$\bar{2}$·8023
0·09375	4952	0·00007520	1·014	0·8128	0·07619	1·230	$\bar{2}$·8819	$\bar{2}$·7919
0·07031	5687	0·00006536	1·010	0·9392	0·06606	1·064	$\bar{2}$·8199	$\bar{2}$·7027
0·0527	6425	0·00005773	1·009	1·1054	0·05825	0·9046	$\bar{2}$·7653	$\bar{2}$·8088
0·03955	7185	0·00005151	1·007	1·3114	0·05186	0·7626	$\bar{2}$·7148	$\bar{2}$·8325
0·02966	8065	0·00004577	1·003	1·5482	0·04591	0·6462	$\bar{2}$·6619	$\bar{2}$·8516
0·02225	9105	0·00004044	1·003	1·8232	0·04057	0·5486	$\bar{2}$·6082	$\bar{2}$·8690
0·01669	10095	0·00003637	1·004	2·1880	0·03653	0·4569	$\bar{2}$·5626	$\bar{2}$·9027
0·01251	11165	0·00003279	1·001	2·622	0·03279	0·3815	$\bar{2}$·5158	$\bar{1}$·9344
0·00939	12355	0·00002952	1·001	3·146	0·02954	0·3179	$\bar{2}$·4704	$\bar{2}$·9681

TABLE II.

Temp. $= 20 \pm 0.05°$. Cell constant $= 0.3776$. Sp. conductivity of water $= 1.035 \times 10^{-6}$ mhos.

C.	R.	κ.	η/η_0.	Λ.	$C\Lambda$.	$1/\Lambda$.	Log $[C\Lambda]$.	Log $[C\Lambda^2]$.
0·125	3464	0·0001080	1·015	0·8766	0·1096	1·141	1·0397	$\bar{2}$·9825
0·09375	3992	0·00009353	1·011	1·0086	0·09452	0·9917	$\bar{2}$·9755	$\bar{2}$·9791
0·07031	4518	0·00008251	1·007	1·1826	0·08318	0·8455	$\bar{2}$·9200	$\bar{2}$·9929
0·0527	5165	0·00007207	1·006	1·3748	0·07246	0·7273	$\bar{2}$·8601	$\bar{2}$·9984
0·03955	5783	0·00006425	1·000	1·6246	0·06424	0·6156	$\bar{2}$·8078	$\bar{1}$·0185
0·02966	6555	0·00005656	1·001	1·9078	0·05659	0·5241	$\bar{2}$·7528	$\bar{1}$·0334
0·02225	7313	0·00005059	0·9993	2·272	0·05056	0·4401	$\bar{2}$·7038	$\bar{1}$·0602
0·01669	8153	0·00004526	1·001	2·716	0·04533	0·3682	$\bar{2}$·6564	$\bar{1}$·0903
0·01251	9132	0·00004030	0·9993	3·218	0·04025	0·3108	$\bar{2}$·6048	$\bar{1}$·1124
0·00939	9893	0·00003713	1·001	3·958	0·03717	0·2526	$\bar{2}$·5702	$\bar{1}$·1677

TABLE III.

Temp. $= 25 \pm 0.05°$. Cell constant $= 0.3776$. Sp. conductivity of water $= 1.11 \times 10^{-6}$ mhos.

C.	R.	κ.	η/η_0.	Λ.	$C\Lambda$.	$1/\Lambda$.	Log $[C\Lambda]$	Log $[C\Lambda^2]$
0·125	2837	0·0001319	1·017	1·0736	0·1342	0·9313	$\bar{1}$·1278	$\bar{1}$·1587
0·09375	3283	0·0001139	1·015	1·2332	0·1155	0·8112	$\bar{1}$·0628	$\bar{1}$·1537
0·07031	3786	0·00009860	1·011	1·4182	0·09970	0·7053	$\bar{2}$·9987	$\bar{1}$·1503
0·0527	4295	0·00008678	1·008	1·6602	0·08748	0·6024	$\bar{2}$·9419	$\bar{1}$·1620
0·03955	4786	0·00007779	1·007	1·9786	0·07807	0·5065	$\bar{2}$·8925	$\bar{1}$·1879
0·02966	5364	0·00006927	1·005	2·346	0·06958	0·4263	$\bar{2}$·8425	$\bar{1}$·2128
0·02225	5983	0·00006200	1·003	2·794	0·06218	0·3580	$\bar{2}$·7936	$\bar{1}$·2398
0·01669	6766	0·00005470	1·002	3·286	0·05486	0·3043	$\bar{2}$·7392	$\bar{1}$·2559
0·01251	7477	0·00004939	1·002	3·954	0·04945	0·2529	$\bar{2}$·6942	$\bar{1}$·2912
0·00939	8314	0·00004430	1·001	4·722	0·04434	0·2117	$\bar{2}$·6468	$\bar{1}$·3209

TABLE IV.

Temp. $= 30 \pm 0.05°$ Cell constant $= 0.3776$. Sp. conductivity of water $= 1.16 \times 10^{-6}$ mhos.

C.	R.	κ	$\dfrac{\eta}{\eta_0}$	Λ.	$C\Lambda$.	$1/\Lambda$.	Log $[C\Lambda]$.	Log $[C\Lambda^2]$.
0·125	2370	0·0001581	1·017	1·2856	0·1607	0·7776	$\bar{1}$·2061	$\bar{1}$·3151
0·09375	2723	0·0001375	1·013	1·4846	0·1392	0·6735	$\bar{1}$·1436	$\bar{1}$·3153
0·07031	3113	0·0001201	1·009	1·7232	0·1212	0·5805	$\bar{1}$·0833	$\bar{1}$·3195
0·0527	3552	0·0001051	1·008	2·010	0·1059	0·4975	$\bar{1}$·0250	$\bar{1}$·3282
0·03955	3915	0·00009528	1·006	2·424	0·09585	0·4126	$\bar{2}$·9816	$\bar{1}$·3661
0·02966	4422	0·00008422	1·002	2·844	0·08435	0·3517	$\bar{2}$·9261	$\bar{1}$·3800
0·02225	4937	0·00007532	1·001	3·388	0·07539	0·2952	$\bar{2}$·8773	$\bar{1}$·4072
0·01669	5498	0·00006751	1·001	4·050	0·06745	0·2469	$\bar{2}$·8290	$\bar{1}$·4365
0·01251	6038	0·00006137	1·001	4·912	0·06145	0·2035	$\bar{2}$·7885	$\bar{1}$·4798
0·00939	6723	0·00005499	1·000	5·856	0·05499	0·1708	$\bar{2}$·7403	$\bar{1}$·5079

TABLE V.

Temp. = 35 ± 0·05°. Cell constant = 0·3776. Sp. conductivity of water = 1·25 × 10^{-6} mhos.

C.	R.	κ.	$\frac{\eta}{\eta_0}$	Λ	CΛ.	1/Λ.	Log [CΛ].	Log [CΛ²]
0·125	1993	0·0001881	1·015	1·5280	0·1909	0·6546	1̄·2809	1̄·4649
0·09375	2282	0·0001642	1·010	1·7694	0·1659	0·5652	1̄·2197	1̄·4675
0·07031	2646	0·0001414	1·007	2·026	0·1425	0·4935	1̄·1538	1̄·4605
0·0527	2956	0·0001264	1·006	2·432	0·1224	0·4111	1̄·0878	1̄·4738
0·03955	3361	0·0001111	1·008	2·830	0·1119	0·3534	1̄·0489	1̄·5007
0·02966	3803	0·00009802	1·006	3·324	0·09858	0·3009	2̄·9938	1̄·5154
0·02225	4174	0·00008918	1·002	4·016	0·08935	0·2491	2̄·9511	1̄·5548
0·01669	4681	0·00007941	1·003	4·772	0·07966	0·2095	2̄·9012	1̄·5799
0·01251	5143	0·00007214	1·001	5·772	0·07221	0·1732	2̄·8586	1̄·6200
0·00939	5702	0·00006495	1·001	6·922	0·06500	0·1445	2̄·8129	1·6531

TABLE VI.

Temp. = 40 ± 0·05°. Cell constant = 0·3776. Sp. conductivity of water = 1·30 × 10^{-6} mhos.

C.	R.	κ.	$\frac{\eta}{\eta_0}$	Λ.	CΛ.	1/Λ.	Log [CΛ].	Log [CΛ²].
0·125	1702	0·0002206	1·016	1·7928	0·2242	0·5577	1̄·3505	1̄·6041
0·09375	1984	0·0001890	1·012	2·040	0·1912	0·4903	1̄·2815	1̄·5911
0·07031	2247	0·0001658	1·008	2·392	0·1682	0·4980	1̄·2259	1̄·6047
0·0527	2564	0·0001459	1·007	2·786	0·1468	0·3590	1̄·1567	1̄·6116
0·03955	2860	0·0001307	1·006	3·324	0·1314	0·3009	1̄·1187	1·6403
0·02966	3193	0·0001169	1·004	3·956	0·1173	0·2527	1̄·0695	1̄·6668
0·02225	3605	0·0001034	1·002	4·656	0·1036	0·2147	1̄·0155	1̄·6836
0·01669	4016	0·00009273	1·002	5·566	0·09292	0·1797	2̄·9681	1̄·7137
0·01251	4418	0·00008416	1·001	6·732	0·08420	0·1486	2̄·9253	1̄·7534
0·00939	4929	0·00007529	1·000	8·022	0·07534	0·1247	2̄·8770	1·7813

TABLE. VII.

Temperature coefficients of conductivity.

Temp.$=15°$.

Temp. coeff. of conductivity for different temp. ranges.

C.	5°.	10°.	15°.	20°.	25°.
0·125	0·04602	0·05065	0·05360	0·05722	0·06061
0·09375	0·04817	0·05171	0·05509	0·05886	0·06039
0·07031	0·05182	0·05099	0·05564	0·05786	0·06189
0·0527	0·04875	0·05019	0·05456	0·06001	0·06082
0·03955	0·04776	0·05088	0·05656	0·05790	0·06139
0·02966	0·04646	0·05154	0·05582	0·05738	0·06223
0·02225	0·04923	0·05326	0·05723	0·06015	0·06218
0·01669	0·04825	0·05019	0·05672	0·05905	0·06175
0·01251	0·04545	0·05081	0·05822	0·06008	0·06270
0·00939	0·05163	0·05010	0·05744	0·06002	0·06200
Mean	0·04835	0·05103	0·05609	0·05885	0·06160

TABLE VIII.

Temperature coefficients of conductivity.

Temp$=20°$.

Temp. coeff. of conductivity for different temp. ranges.

C.	5°.	10°.	15°.	20°.
0·125	0·04494	0·04666	0·04955	0·05226
0·09375	0·04455	0·04722	0·05031	0·05114
0·07031	*0·03984	0·04581	0·04753	0·05112
0·0527	0·04151	0·04619	0·05126	0·05133
0·03955	0·04358	0·04920	•0·04945	0·05231
0·02966	0·04593	0·04907	0·04946	0·05367
0·02225	0·04595	0·04911	0·05117	0·05247
0·01669	0·04198	0·04912	0.05048	0·05247
0·01251	0·04574	0·05265	0·05290	0·05461
0·00939	*0·03860	0·04796	0·04992	0·05134
Mean	0·04427	0·04830	0·05020	0·05227

* These observations are rejected due to accidental errors.

TABLE IX.

Temperature coefficients of conductivity.

Temp. $= 25°$.

C.	Temp. coeff. for different temp. ranges.			C.	Temp. coeff. for different temp. ranges,		
	5°.	10°.	15°.		5°.	10°.	15°.
0·125	0·03949	0·04233	0·04465	0·02966	0·04245	0·04169	0·04575
0·09375	0·04079	0·04350	0·04362	0·02225	0·04252	0·04374	0·04443
0·07031	0·04301	0·04286	0·04578	0·01669	0·04649	0·04523	0·04625
0·0527	0·04214	0·04649	0·04521	0·01251	*0·04846	0·04598	0·04685
0·03955	0·04502	0·04302	0·04532	0·00939	*0·04803	0·04659	0·04659
				Mean	0·04274	0·04414	0·04546

* Rejected due to accidental errors.

TABLE X.

Temperature coefficients for different ranges.

C.	At 30°. Temp. coeff. for a range of		At 35° Temp. coeff. for a range of	C.	At 30°. Temp. coeff. for a range of		At 35°. Temp. coeff. for a range of
	5°.	10°.	5°.		5°.	10°.	5°.
0·125	0·03770	0·03946	0·03466	0·02966	0·03375	0·03910	0·03803
0·09375	0·03835	0·03741	0·03059	0·02225	0·03708	0·03744	0·03188
0·07031	0·03517	0·03883	0·03613	0·01669	0·03565	0·03743	0·03328
0·0527	0·04199	0·03861	0·02911	0·01251	0·03501	0·03705	0·03326
0·03955	0·03350	0·03713	0·03490	0·00939	0·03641	0·03699	0·03178
				Mean	0·03646	0·03795	0·03336

Table XI.

Viscosities of $HgCl_2$ *solutions at different temperatures.*

η_t in absolute units.

C.	$\eta_{15°}$.	$\eta_{20°}$.	$\eta_{25°}$.	$\eta_{30°}$.	$\eta_{35°}$.	$\eta_{40°}$.
0·125	0·01190	0·01039	0·0091995	0·0081936	0·007367	0·006692
1·0969	$\overline{2}$·0755	$\overline{2}$·0165	$\overline{3}$·9638	$\overline{3}$·9135	$\overline{3}$·8673	$\overline{3}$·8255
0·09375	0·01184	0·01035	0·0091775	0·0081612	0·0073308	0·006665
$\overline{2}$·9719	$\overline{2}$·0734	$\overline{2}$·0149	$\overline{3}$·9628	$\overline{3}$·9118	$\overline{3}$·8652	$\overline{3}$·8238
0·07031	0·01180	0·01031	0·0091417	0·0081356	0·0073028	0·006637
$\overline{2}$·8471	$\overline{2}$·0719	$\overline{2}$·0132	$\overline{3}$·9610	$\overline{3}$·9104	$\overline{3}$·8635	$\overline{3}$·8220
0·0527	0·01179	0·010294	0·009119	0·008123	0·007298	0·006631
$\overline{2}$·7218	$\overline{2}$·0716	$\overline{2}$·0125	$\overline{3}$·9599	$\overline{3}$·9098	$\overline{3}$·8632	$\overline{3}$·8216
0·03955	0·011765	0·01024	0·0091003	0·008110	0·007312	0·006625
$\overline{2}$·5971	$\overline{2}$·0707	$\overline{2}$·0103	$\overline{3}$·9590	$\overline{3}$·9090	$\overline{3}$·8640	$\overline{3}$·8212
0·02966	0·011723	0·010243	0·0090893	0·008078	0·007298	0·006613
$\overline{2}$·4722	$\overline{2}$·0691	$\overline{2}$·0104	$\overline{3}$·9585	$\overline{3}$·9073	$\overline{3}$·8632	$\overline{3}$·8204
0·02225	0·01172	0·01023	0·009072	0·008071	0·0072738	0·006500
$\overline{2}$·3474	$\overline{2}$·0690	$\overline{2}$·0098	$\overline{3}$·9577	$\overline{3}$·9070	$\overline{3}$·8617	$\overline{3}$·8195
0·01669	0·01173	0·01025	0·009065	0·008071	0·007278	0·006597
$\overline{2}$·2225	$\overline{2}$·0693	$\overline{2}$·0107	$\overline{3}$·9573	$\overline{3}$·9070	$\overline{3}$·8620	$\overline{3}$·8194
0·01251	0·011693	0·01023	0·009063	0·008072	0·0072656	0·006594
$\overline{2}$·0972	$\overline{2}$·0680	$\overline{2}$·0098	$\overline{3}$·9572	$\overline{3}$·9070	$\overline{3}$·8613	$\overline{3}$·8192
0·00939	0·01169	0·010246	0·009052	0·008062	0·007263	0·006591
$\overline{3}$·9727	$\overline{2}$·0679	$\overline{2}$·0105	$\overline{3}$·9567	$\overline{3}$·9064	$\overline{3}$·8611	$\overline{3}$·8190
Water	0·011683	0·010235	0·009043	0·0080626	0·007256	0·0065885
	$\overline{2}$·0678	$\overline{2}$·0102	$\overline{3}$·9563	$\overline{3}$·9064	$\overline{3}$·8606	$\overline{3}$·8188

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TABLE XII.

Temperature coefficients of viscosity.

Temp. = 15°.

Temp. coeff. of viscosity for different temp. ranges

C.	5°.	10°.	15°.	20°.	25°.
0·125	0·02538	0·02270	0·02076	0·01904	0·01751
0·09375	0·02517	0·02249	0·02071	0·01904	0·0174ᵠ
0·07031	0·02525	0·02253	0·02070	0·01905	0·01750
0·0527	0·02538	0·02266	0·02073	0·01905	0·01750
0·03955	0·02592	0·02266	0·02071	0·01892	0·01748
0·02966	0·02524	0·02247	0·02073	0 01887	0·01744
0·02225	0·02543	0·02259	0·02075	0·01897	0·01748
0·01669	0·02523	0·02272	0·02080	0·01898	0·01750
0·01251	0·02502	0·02249	0·02065	0·01893	0·01745
0·00939	0·02471	0·02257	0·02069	0·01893	0·01745
Mean 0·02527	0·02259	0·02072	0·01898	0·01748	

TABLE XIII.

Temperature coefficients of viscosity.

Temp. = 20°.

Temp. coeff. of viscosity for different temp. ranges.

C.	5°.	10°.	15°.	20°.
0·125	0·02292	0·02113	0·01939	0·01779
0·09375	0·02262	0·02114	0·01945	0 01780
0·07031	0·02267	0·02109	0·01945	0·01781
0·0527	0·02283	0·02109	0·01940	0·01779
0·03955	0·02226	0·02080	0·01906	0·01765
0·02966	0·02253	0·02113	0·01917	0·01772
0·02225	0·02263	0·02111	0·01927	0·01774
0·01669	0·02312	0·02126	0·01933	0·01782
0·01251	0·02281	0·02110	0·01932	0·01777
0·00939	0·02331	0·02131	0·01941	0·01783
Mean 0·02277	0·02112	0·019325	0·01777	

TABLE XIV.

Temperature coefficients of viscosity.

Temp. = 25°.

C.	Temp. coeff. for ranges			C.	Temp. coeff. for ranges		
	5°.	10°.	15°.		5°.	10°.	15°.
0.125	0.02187	0.01992	0.01818	0.02966	0.02225	0.01971	0.01817
0.09375	0.02215	0.02012	0.01825	0.02225	0.02207	0.01983	0.01817
0.07031	0.02201	0.02011	0.01827	0.01669	0.02194	0.01972	0.01815
0.0527	0.02184	0.01997	0.01819	0.01251	0.02187	0.01984	0.01817
0.03955	0.02176	0.01965	0.01813	0.00939	0.02187	0.01976	0.01812
				Mean	0.02196	0.01986	0.01818

TABLE XV.
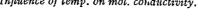
Temperature coefficients of viscosity.
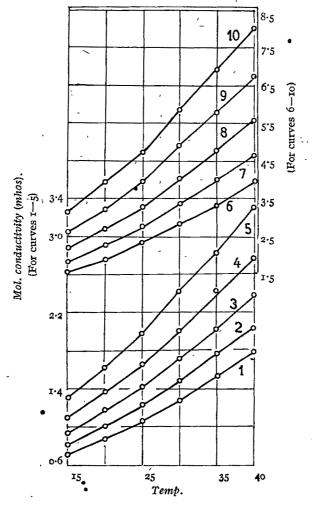
C.	Temp 30°.		Temp. 35°.	C.	Temp. 30°.		Temp. 35°.
	Temp. coeff. for 5° range.				Temp. coeff. for 5° range.		
	5°.	10°.	5°.		5°.	10.	5°.
0.125	0.02018	0.01832	0.01832	0.02966	0.01936	0.01813	0.01877
0.09375	0.02035	0.01833	0.01817	0.02225	0.01975	0.01823	0.01852
0.07031	0.02047	0.01842	0.01824	0.01669	0.01965	0.01827	0.01872
0.0527	0.02032	0.01837	0.01828	0.01251	0.01998	0.01827	0.01849
0.03955	0.01968	0.01837	0.01879	0.00939	0.01982	0.01825	0.01850
				Mean	0.01996	0.018296	0.01848

DISCUSSION.

The foregoing results show that within the limits of temperature investigated, Λ, the molecular conductivity of $HgCl_2$ in aqueous system, increases steadily with rise in T, the temperature (column 5, Tables I.-VI). The Λ-T curves, corresponding to ten different dilutions shown in Fig. 1,

Fig. 1.

Influence of temp. on mol. conductivity.

show also that in all these cases the curve is inclined towards the Λ-axis and that this tendency becomes more pronounced as the dilution is increased. Data shown under column 3, in Tables I-VI indicate that HgCl₂ behaves as an extremely weak electrolyte, almost a non-electrolyte as is obvious from the exceedingly low order of the specific conductivities measured for even fairly concentrated solutions which are in close agreement with the results of Hampe (*loc. cit.*), Faraday (*loc. cit.*), Morse (*loc. cit.*), and others. The observed increase in the conductivity with the rise in temperature is partly explained

by our results that with the rise in temperature, the viscosity of the medium decreases; consequently, the mobility of the relevant ions would increase, which is in agreements with the findings of Kohlrausch (loc. cit.), Noyes, Melcher and Cooper (loc. cit.), Bousfield and Lowry (loc. cit.), Jones (loc. cit.) and others. Our result, that the departure from the linearity of the Λ-T curve increases with the dilution may in part be attributed to the increased hydrolysis of $HgCl_2$ with dilution. Ley (loc. cit.) has studied this in some detail. His results show that the hydrolysis of aqueous $HgCl_2$ is quite sensible even at $6°$, its extent increases with dilution and temperature. The chief result of increased hydrolysis is to increase the hydrogen ion concentration and hence the corresponding conductivity. It is therefore to be anticipated that the departure from the linear relationship of the Λ-T curve, indicative of an extra rise in conductivity, may be produced as a result of increased hydrolysis. Our experimental results are in close accord with this deduction.
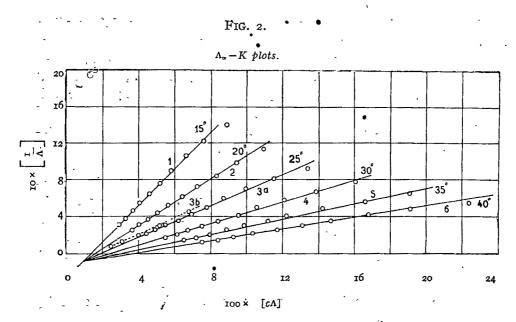
No quantitative information is available in the literature regarding the values for Λ_∞, the molecular conductivity for $HgCl_2$ at infinite dilution at different temperatures to enable us to calculate the degrees of ionisation α, and also the dissociation constant, K, by the application of Ostwald's dilution law. An attempt has therefore, been made to evaluate Λ_∞ and K by the graphical method developed by Kraus and Bray (J. Amer. Chem. Soc., 1913, 35, 1315) and found to be utilisable for a surprisingly large number of electrolytes in both aqueous and non-aqueous solvents. The mass law expression as applied to weak electrolytes, undergoing binary dissociation gives

$$K = \frac{\Lambda^2 . C}{(\Lambda_\infty - \Lambda)\Lambda_\infty}. \qquad \qquad \text{...} \quad (i)$$

The equation (i) after rearranging reduces finally to :

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_\infty} + \frac{1}{K . \Lambda_\infty^2} (C\Lambda). \qquad \qquad \text{...} \quad (ii)$$

The plot of $C\Lambda$ (along abscissa) against $1/\Lambda$ (along the ordinate) gives a straight line; the intercept on the ordinate gives $1/\Lambda_\infty$ from which Λ_∞ and finally K, can easily be computed; these curves, Kraus and Bray have designated as "$\Lambda_\infty - K$, plots". With a view to finding how far the equation

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FIG. 2.

$\Lambda_\infty - K$ plots.

(ii) holds in the case of $HgCl_2$, these plots are shown in Fig. 2 after appropriate calculations from our data (Table I-VI). The curves, showing $\Lambda_\infty - K$ plots (Fig. 2, curves 1-6, at different temperatures), are all straight lines but give the intercepts on the negative side of the ordinate, to which, at present no physical meaning can be attached. It is, however, very significant that all these curves pass through a common point of intersection. For the sake of comparison Ley's data (loc. cit.) at 25° are also shown by a dotted curve [3 (b), Fig. 2] ; his curve is slightly above ours on account of the fact that $1/\Lambda$ values of Ley were not, while our values are corrected for viscosity. This suggests that either, (a) the equation (ii), which holds for an electrolyte undergoing binary dissociation, may not adequately express the dissociation of mercuric chloride or (b), possibly, mercuric chloride does not belong to the type of electrolyte which undergoes simple binary dissociation considered in Kraus and Bray's procedure. Sherril (loc. cit.) calculated the ionisation constant K for
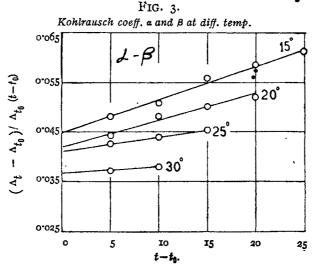
$$Hg + 2Cl' = HgCl_2 \ i.e., \ (Hg) \times (Cl')^2 = K(HgCl_2)$$

by E.M.F., and solubility data and partition of $HgCl_2$ between toluene and water, and toluene and mercuric nitrate solution. K for ternary dissociation was found to vary in the range 1×10^{-14} and 1.5×10^{-14}. The existence of the ions $(HgCl')$ was established by Morse (loc. cit.) from the transport number measurements so that the ionisation of $HgCl_2$ $HgCl_2 = Hg'' + 2Cl'$, takes place in stages :

$$HgCl_2 = HgCl^{\cdot} + Cl' \; ; \; K_1 = \frac{[HgCl^{\cdot}] \times [Cl']}{[HgCl_2]} \qquad \ldots \; (a$$

$$HgCl^{\cdot} = Hg^{\cdot\cdot} + Cl' \; ; \; K_2 = \frac{[Hg^{\cdot\cdot}] \times [Cl']}{[HgCl^{\cdot}]} \qquad \ldots \; (b$$

The ionisation constants K_1 and K_2 for (a) and (b) were found to be $2\cdot8 \times 10^{-7}$ and $3\cdot5 \times 10^{-8}$ respectively. According to Luther, however, solution of $HgCl_2$, saturated at $25°$, contains the following constituents expressed in moles per litre : $(HgCl_2) = 0\cdot26$; $(HgCl^{\cdot}) = 0\cdot00015$; $(H^{\cdot})$ $= 0\cdot00033$; $(Cl') = 0\cdot00048$; $(Hg^{\cdot\cdot}) = 10^{-8}$; $(HgCl''_4) = 5 \times 10^{-6}$. It is therefore, to be anticipated that the dissociation of $HgCl_2$ may not obey the simple binary dissociation law- a deduction in agreement with our results showing the departure in $\Lambda_\infty - K$ plots as well as $\log (C\Lambda) - \log (C\Lambda^2)$ plots. The possible disturbing factors may now be considered : (i) The dissociation might proceed in stages : (a) $HgCl_2 = HgCl^{\cdot} + Cl'$; (b) $HgCl^{\cdot}$ $= Hg^{\cdot\cdot} + Cl'$; both the reactions (a) and (b) obey binary dissociation law and are of the same order ; (ii) Causes leading to hydration or solvation, and (iii) hydrolysis leading to the formation of free HCl which dissociates into $H^{\cdot}$ and Cl'. Discordant views prevail in regard to the mechanism of the hydrolysis of $HgCl_2$. Ley $(loc.\ cit.)$ suggested that the reaction proceeds as either, $2HgCl_2 + H_2O = [HgCl_2]_2O + 2H^{\cdot} + 2Cl'$; or else, $HgCl_2 + H_2O$ $= HgCl (OH) + H^{\cdot} + Cl'$. Kahlenberg's results $(loc.\ cit.)$ favour the first hypothesis. Fischer and Breiger $(Kolloid\ Z.,$ 1910, 7, 196) suggested that $HgCl_2$ in aqueous solution is split up into HCl and a colloid. Thümmel $(Arch.\ Pharm.,$ 1885, 223, 929) adduced evidence to show that aqueous $HgCl_2$ behaves as containing an acid $H_2(HgOCl_2)$ because of the peculiar hydrolytic changes.

FIG. 3.

Kohlrausch coeff. α and β at diff. temp.

It is interesting to consider the influence of temperature on the conductance of $HgCl_2$ (cf. Table VII-X). This is seen to be far higher than what obtains usually in the case of normal electrolytes A survey of the data in the literature shows that the temperature coefficient of conductivity is about 1·6 % for strong acids, 2·2% for binary electrolytes, and 2·5% for ternary electrolytes. Our result that this quantity for $HgCl_2$ varies in the range 3·8 to 6·2% suggests that either its ionisation is of a higher order involving a complex aggregate which gives ions, or else it is a typical weak electrolyte, it being known that the influence of temperature in increasing the conductivity is more marked in their case than with strong electrolytes, or what is more probable, both these factors might operate The fact that the temperature coefficient of conductivity for aqueous $HgCl_2$ alters only slightly with dilution may be taken as evidence to show that $HgCl_2$ in aqueous solutions does not form hydrates, possibly because of its weak electrolytic nature.   Jones (*Carnegie Inst. of Washington* 1907, Pb 60) and collaborators have adduced very considerable evidence to show that there is no possibility of hydration taking place in the case of non-electrolytes, because of the comparative scarcity of the charged ions, which produce hydration due to the strong electrostatic forces of attraction between the charged ions and the dipoler water molecules.

It is interesting to point out that our data showing the effect of temperature on the conductivity of $HgCl_2$, satisfy Kohlrausch's relation :

$$\Lambda_t = \Lambda_{t_0}[1 + a(t - t_0) + \beta(t - t_0)^2]$$
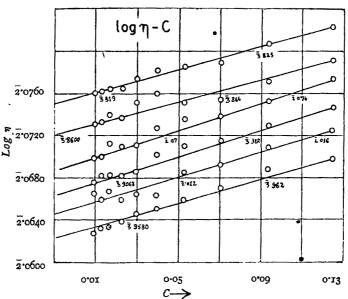
as is shown by the straight line curves (cf. Fig. 3, a, β plot) obtained by plotting

$$\frac{\Lambda_t - \Lambda_{t_0}}{\Lambda_{t_0}(t - t_0)}$$

on the ordinate, against $(t - t_0)$ on the abscissa, the intercept on the ordinate, and the slope of the curve give respectively the values of a and β, the coefficients appearing in the above equation. The coefficients are complicated functions of temperature, their values decreasing with rise in temperature.   Our results showing the decrease of temperature co-coefficients of conductance with the corresponding fall in the values of efficients a and β, with rise of temperature can be explained on the assumption that with rise in temperature the association of water becomes less (cf. Jones and West, *loc. cit.*, Ramsay and Shields, *loc. cit.*) and thus brings about the lowering in the ionising power of the solvent medium (cf. Dutoit and Aston). The fact that the dissociation decreases

with rise of temperature is also in agreement with the conclusions that can be drawn from the results of Vonwiller (*loc. cit.*) showing a decrease in the dielectric constant of water with rise of temperature, and the Thomson-Nernst's rule (*Phil. Mag.*, 1893, **36**, 313 ; *Z. physikal. Chem.*, 1894, **13**, 535 ; *cf.* Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 21 ; 1933, **55**, 476, 1019) connecting the dissociating power of a solvent with its dielectric constant. That the temperature coefficients of conductivity decrease with rise of temperature is in harmony with the views of Bousfield and Lowry (*loc. cit.*) on other independent grounds.
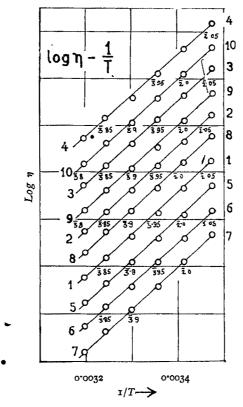
FIG. 4.

Influence of conc. on viscosity at diff. temp.

Our results on the viscosities of aqueous $HgCl_2$ for different concentrations and at different temperatures (*cf.* Table XI) show that the viscosity coefficient at any temperature increases with the concentration, especially in fairly strong solutions ; in very dilute solutions difficulties arise owing to the fact that the viscosity of the solution varies from that of the pure solvent (water), to an extent which comes within the range of the experimental error. The above variations of viscosity with concentration and temperature can be adequately expressed by the expressions, $\log \eta = kC$ and $\log \eta = \dfrac{B}{T} - A$, where C is the volume concentration in moles per litre, T, the absolute temperature, k, B, and A being constants as is shown by

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straight line curves of log η against C . (*cf.* curves 1-6 in Fig. 4) and against $\frac{1}{T}$ (curves 1-10 in Fig. 5) (*cf.* Berl and Umstätter and Karrer, *loc. cit.*.)
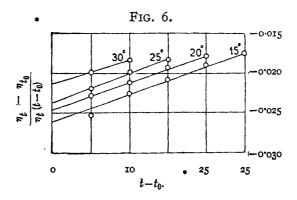
FIG. 5.

Influence of temp. on viscosity for diff. conc.

Our results on the temperature coefficients of viscosity of aqueous $HgCl_2$ (*cf.* Tables XII-XV) at different temperature ranges, show that the temperature coefficent, $\frac{\eta_t - \eta_{t_o}}{\eta_{t_o}(t-t_o)}$ increases (algebraically) with rise in temperature. It is, however, interesting to point out that the temperature coefficients of viscosity of $HgCl_2$ solutions are almost equal to those of the pure solvent, water. It is also seen that the temperature coefficient of viscosity of the solvent (water) remains unaltered despite the varying concentration of $HgCl_2$ present in the system. Our data showing the effect of temperature on the viscosity of aqueous $HgCl_2$ satisfy the relation (*cf.* Bousfield and Lowry, *loc. cit.*), $\eta_t = \eta_{t_o}[1 + \alpha(t-t_o) + \beta(t-t_o)^2]$ as is seen from the straight

line graphs obtained by plotting $\dfrac{\eta_t - \eta_{t_o}}{\eta_{t_o}(t - t_o)}$ on the ordinate against $(t - t_o)$ on the abscissa (cf. curves 1-4, α, β plots in Fig. 6). The values of the coefficients α and β, the former being negative and the latter positive,

FIG. 6.

appearing in the above equation, have been graphically evaluated. The intercept on the ordinate and the slope of the curve give respectively the values of α and β.

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STUDIES IN THE SESQUITERPENE SERIES. PART I. SYNTHESIS OF THE TRIETHYL ESTER OF $C_9H_{15}(CO_2H)_3$, OBTAINED FROM SELINENES.*

By Phanindra Chandra Dutta.

A synthetic route has been developed for the synthesis of the tricarboxylic acid which has been obtained by the oxidation of selinenes. This method again offers the possibilities for the extension of the same for the synthesis of the naturally occurring selinenes and related bodies. One of the salient points of the scheme is the introduction of the carboxyl group at the required position in the cyclohexane ring through the condensation of oxalic ester according to the " Principle of Vinylogy "

As much of the evidence for the existence of the angular methyl group in the sesquiterpenes is indirect, being based on the isoprene rule, it appeared that the synthetical experiments in the eudesmol group are necessary to supplement the analytical evidences of Ruzicka and his co-workers. The first successful synthetic attempt in this group is due to Simonsen (*J. Chem. Soc.*, 1936, 1138), who prepared a hydrogenated sesquiterpene ketone belonging to the eudesmol group.

Ruzicka, Koolhaus and Wing (*Helv. Chim. Acta*, 1931, 14, 1151, 1171) have shown that the sesquiterpenes of the selinene group belong to the *cis*-decalin series. It is known that the *trans*-fusion of one cyclohexane ring to another in the *ortho*-position is stable. The *cis*-fusion results in an unstable arrangement which easily isomerises to the *trans*-form at high temperatures. Moreover, physical measurements, *e.g.* heat of combustion, etc., also prove the *cis*-form to be the less stable form (Roth and Lasse, *Annalen*, 1925, 441, 48). The stability of the *cis*-linking arises through the presence of an angular methyl group. Similarly, in the bi*cyclo*-octane series, methyl group stabilises the unstable 8-methyl-bi*cyclo*-octane derivatives (Wieland and Dane, *J. physiol. Chem.*, 1933, 216, 91). These observations have led Hückel to the view that the strain theory cannot be applied in a simple manner to the bi*cyclo* systems (Mills, " Reports of the Fourth Solvay Conference," 1931, p. 16). Hence to realise an actual synthesis of these bodies the possibilities of the formation of various isomers at intermediate stages should be avoided so that the disturbing factor of stereoisomerism is minimised to an appreciable extent.

A possible method has now been developed for the synthesis of selinic acid (Semmler *et al.*, *Ber.*, 1912, **45**, 3031, 3725 ; 1913, **46**, 599) which has been tentatively formulated by Ruzicka (*Helv. Chim. Acta*, 1922, **5**, 345) as (I).

It is evident that it can exist in four stereochemical forms and its actual synthesis will also finally establish the presence of the angular methyl group with all its stereochemical implications.

Chloromethyl ether does not condense with *o*-methyl*cyclo*hexanone in presence of sodamide in ethereal solution (*cf.* Haller and Cornubert, *Bull. Soc. Chim.*, 1927, **41**, 367) and hence the lactone (II, *n*=1) could not be prepared, where the two rings in the lactone (II, *n*=1) should have *cis*-locking (*cf.* Hückel, *Annalen*, 1934, **514**, 240; Linstead, *J. Chem. Soc.*, 1936, 481). By this procedure, two possibilities out of four are ruled out and we are left only with the following possibilities :

(*i*)   COOH and the lactone group in *cis*-configuration,

(*ii*)   COOH and the lactone group in *trans*-configuration.

Further, as the hydroxy-dicarboxylic acid corresponding to the lactone acid (II, *n*=1 ; R=H) is a substituted *iso*phthalic acid, the two carboxyl groups in it are interconvertible under standard conditions. It may be mentioned in this connection that there is no reference in the existing literature as regards the actual stereoisomerism of the *iso*propylene group with respect to the angular methyl group or the other ring of the decalin system in the selinenes and related bodies.

Attempts to condense ethoxyethyl chloride with *o*-methyl*cyclo*hexanone failed to give (II, *n*=2) but ethoxyethyl iodide smoothly reacts with the ketone under the usual conditions. As the product of condensation consists mainly of 1 : 1-disubstituted *cyclo*hexan-2-one and a little of the 1 : 3-isomer, it is purified according to Ruzicka's method (*Helv. Chim. Acta*, 1931, **14**, 1169) by condensing with oxalic ester and then Simonsen's modification (*J. Chem. Soc.*, 1936, 1140) being followed for the isolation of the oxalo-derivative. The oxalo-derivative, thus obtained, is hydrolysed with baryta and the ketone (III) regenerated and converted into the related cyanohydrin in a quantitative yield with liquid hydrocyanic acid. The cyanohydrin is unusually stable, confirming Lapworth and Manske's views on the effect of α-alkylation (*J. Chem. Soc.*, 1930, 1976). The cyanohydrin is dehydrated with thionyl chloride and pyridine. The unsaturated nitrile (IV) is freed from sulphur by heating with precipitated copper in benzene. This method is decidedly an advantage over Simonsen's procedure of removing sulphur compounds by allowing to stand over aluminium-mercury couple for

several days. The purified unsaturated nitrile condenses smoothly with ethyl oxalate in presence of potassium ethoxide (Lapworth, *J. Chem. Soc.*, 1901, **79**, 1265; Kuhn *et al.*, *Ber.*, 1937, **70**, 70, *et seq.*) and the yield of the condensation product is improved by using anhydrous pyridine as diluent (*cf. Ber.*, 1937, **70**, 1148). The condensation product (V), isolated by vacuum distillation, is hydrolysed in methyl alcoholic solution with potassium hydroxide solution.

The pyruvic acid has been oxidised with hydrogen peroxide in pyridine solution in satisfactory yield, the other usual methods proving unsuccessful. The unsaturated cyano-acid, thus obtained, is reduced with sodium amalgam and isolated as the methyl ester (VI) after esterification. Hydrolysis of the cyano group and simultaneous de-ethoxylation have been carried out with hydrobromic acid. The product may be the lactonic acid II, $n=1$; R=H) together with the corresponding bromodibasic acid. Consequently the mixture is directly treated with phosphorus pentabromide in the cold and subsequently treated with alcohol. From the reaction mixture the ester (VII, R=Br) is isolated in moderate yield together with a lower boiling fraction, which is most probably the lactonic ester (II $n=1$; R=Et) ; the structure could not be definitely established, yield being too small. Replacement of the bromine atom by a cyano group has been carried out by the method of Rydon (*J. Chem. Soc.*, 1937, 1341). The cyano compound is directly esterified and the triester (VIII, R=CO_2Et) has been isolated in very poor yield. Further work is in progress.

The bromo-ester (VII, R=Br) can be condensed with ethyl malonate for the synthesis of 9-methyldecalin systems which would lead to hydrogenated selinenes.

(I)

(II)

(III)

(IV)

CH$_2$
H$_2$C $\quad$ C $\diagdown$ Me
$\qquad\qquad$ CH$_2\cdot$CH$_2\cdot$OEt
EtO$_2$C$\cdot$OC$\cdot$HC $\quad$ C$\cdot$CN
CH

(V)

CH$_2$
H$_2$C $\quad$ C $\diagdown$ Me
$\qquad\qquad$ CH$_2\cdot$CH$_2\cdot$OEt
MeO$_2$C$\cdot$HC $\quad$ CH$\cdot$CN
CH$_2$

(VI)

CH$_2$
H$_2$C $\quad$ C $\diagdown$ Me
$\qquad\qquad$ CH$_2\cdot$CH$_2$R
EtO$_2$C$\cdot$HC $\quad$ CH$\cdot$CO$_2$Et
CH$_2$

(VII)

EXPERIMENTAL.

β-*Ethoxyethyl Chloride*·—To a mixture of glycol monoethyl ether (180 g.) and pyridine (160 g.), cooled in ice, was added slowly with constant shaking thionyl chloride (250 g.). After standing overnight, the mixture was heated on the water-bath for 1 hour. After cooling, the chloride was decanted off from pyridine hydrochloride and the latter, after decomposition with ice, was extracted with ether. The combined ethereal extracts and the chloride were washed with acid and alkali, and fractionated, b.p. 108-10°. It was converted into iodide, b.p. 151-54°, by refluxing with sodium iodide in alcoholic solution in the usual way.

1-*Methyl*-1-β-*ethoxyethylcyclohexan-2-one* (III).—A mixture of 2-methyl*cyclo*hexanone (112 g.) and finely powdered sodamide (45 g.) in ether (1200 c c.) was heated under reflux with stirring for 5 hours. After 2 hours the volume of ether was gradually reduced to about 500 c.c., the mixture cooled in ice and ethoxyethyl iodide (200 g.) added in the course of 50 minutes. The temperature was gradually raised and the solution refluxed for another 5 hours, in such a manner that most of the ether evaporated off, for condensation with ethoxyethyl iodide proceeded better in concentrated solution. After standing overnight, the residue was decomposed with ice,

the ethereal layer separated and the aqueous portion extracted with ether. The ethereal solution was dried and low boiling fractions were removed at atmospheric pressure. From the residue, the fraction boiling at 95-110°/8 mm. was collected. On redistillation it had b.p. 100-105°/5 mm. (mainly 103°/6 mm.), yield 75 g. (Found : C, 71·4; H, 10·7. $C_{11}H_{20}O_2$ requires C, 71·6; H, 10·8 per cent).

To a solution of sodium (7·6 g.) in alcohol (100 c.c.) cooled in a freezing mixture a cooled mixture of the above ketone (53 g.) and ethyl oxalate (42·4 c.c.) was added with thorough shaking, when a thick reddish brown solution was obtained. After standing overnight, the product was poured into ice and the alkaline solution was extracted with ether. The crude reddish oil from ether was hydrolysed on the water-bath with barium hydroxide (128 g.) and water (600 c.c.) for 4 hours. The precipitated solids were collected and washed with ether. The aqueous portion was also extracted with ether. The combined ethereal extract was dried and the solvent removed when the ketone was obtained. The precipitated barium salts were decomposed with ice and hydrochloric acid, barium chloride filtered off and the aqueous portion was thoroughly extracted with ether. The reddish oil, left after removal of the solvent, was again hydrolysed with baryta solution. The over-all yield of the ketone is 35 g., b.p 100°/6 mm. (Found: C, 71·8; H, 10·42. $C_{11}H_{20}O_2$ requires C, 71·6 ; H, 10·8 per cent).

The neutral fraction from the oxalic ester condensation was worked up in the usual way and only a small quantity of ketone was obtained which showed that the condensation had resulted mainly in the production of the 1 : 1-isomer.

The *semicarbazone*, prepared in the usual way, crystallised from dilute alcohol in sandy crystals, m.p. 122°. (Found : N, 17·5. $C_{12}H_{23}O_2N_3$ requires N, 17·0 per cent).

1-Methyl-1-β-ethoxyethylcyclohexanone-2-cyanohydrin.— The above ketone (12 g.), to which a drop of potassium cyanide solution had been added as a condensing agent, was cooled to −10° and hydrogen cyanide, generated from potassium cyanide (45 g.) and dilute sulphuric acid (45 c.c. H_2SO_4 ; 60 c.c. H_2O), was slowly passed into the ketone in the course of 1 hour. After standing overnight at 0° the solution was acidified with ice-cold sulphuric acid and a current of air passed through it to remove unreacted hydrogen cyanide. Finally it was extracted with ether, the extract dried over sodium sulphate and after the addition of a drop of sulphuric acid

.distilled, 147°/9 mm., yield 13 g. (Found : N, 7·2. $C_{12}H_{21}O_2N$ requires N, 6·7 per cent).

1-Methyl-1-β-ethoxyethyl-2-cyano-Δ^2-cyclohexene (IV).—A mixture of pyridine (5·9 c.c.) and the cyanohydrin (5 g.) was cooled in a freezing mixture and thionyl chloride (6 c.c.) was gradually added with thorough shaking and the solution was allowed to stand overnight when two layers were formed. The mixture was heated on the water-bath for 2 hours, cooled and the upper layer extracted with sodium-dried ether to avoid the formation of persistent emulsion. The plastic mass left was decomposed with ice and hydrochloric acid and again extracted with ether. The combined ethereal extracts were thoroughly washed with water, acid and alkali. After drying over calcium chloride, the solvent was removed and the residue distilled at 122-27°/7 mm. and contained much dissolved sulphur which was removed by boiling in dry benzene solution with precipitated copper for a few hours. From the benzene filtrate the nitrile was obtained as a clear colourless oil, b.p. 118-20°/5 mm., yield 7·5 g. from two similar experiments. The dehydration takes place better when small quantities were employed. (Found : N, 7·6. $C_{12}H_{19}ON$ requires N, 7·25 per cent).

Ethyl (1-*Methyl-1-β-ethoxyethyl-2-cyano-Δ^2-cyclohexenoyl*)-*formate* (V).—Potassium (13·8 g.), placed under ether, was treated with absolute alcohol (70 c.c. freshly distilled over calcium) and heated under reflux until complete solution. A portion of the ether was evaporated off through the condenser avoiding formation of solid crusts. After cooling in a freezing mixture, ice-cold pure ethyl oxalate (25 c.c.) was added and the mixture allowed to stand for 10 minutes. To the mixture a cooled solution of the nitrile (31 g.) in freshly distilled pyridine (60 c.c.) was added slowly with shaking. The solution became at first deep violet and then blood-red. After standing in ice-chest for 36 hours the solution was decomposed with ice when the potassium salt separated, which dissolved on further dilution. The reddish alkaline solution was extracted with ether whence the unsaturated nitrile (8 g.) was recovered. The alkaline solution furnished a heavy oil on acidification with dilute sulphuric acid which was extracted with ether and the ethereal extract was washed with water and dried. The residue from ether distilled at 168-70°/2 mm. as a viscous gum having a light yellow colour. It gave a deep violet ferric reaction in alcoholic solution, yield 24 g (Found : C, 65·2 ; H, 7·5. $C_{16}H_{23}O_4N$ requires C, 65·46 ; H, 7·8 per cent).

Methyl 1-Methyl-1-β-ethoxyethyl-2-cyanocyclohexane-4-carboxylate (VI). —To the cyanoketo-ester (V, 16 g.), dissolved in methyl alcohol (50 c.c.), was

added with shaking a solution of sodium hydroxide (9·5 g.) in water (75 c.c.), the mixture became hot and was allowed to stand at room temperature for 2 days and then refluxed for 1 hour on the steam-bath. After acidification with ice-cold sulphuric acid, the precipitated oil was extracted with ether, the extract dried in vacuum for a day and the resulting reddish mass dissolved in pyridine (100 c.c.). Hydrogen peroxide (5 c.c. of 0·012 g. of oxygen per c.c.) was added and the temperature was gradually raised to 60° and a further quantity (4 c.c.) of hydrogen peroxide added. After keeping the mixture at 60° for 1 hour, it was poured into ice-cold sulphuric acid and extracted twice with ether The residue from ether was reduced with sodium amalgam (3%, 700 g.), the mixture being kept nearly neutral with sulphuric acid. The acidic solution was extracted with ether, dried over sodium sulphate, and the gummy residue (11·5 g.) from ether dried in vacuum. It was dissolved in methyl alcohol (100 c.c.) and esterified with hydrogen chloride and the product isolated in the usual way, b.p. 145-48°/2 mm., yield 8 g. (Found : C, 66·7 ; H, 8·6. $C_{14}H_{23}O_3N$ requires C, 66·4 ; H, 9·01 per cent).

Ethyl 2-Methyl-1-(β-biomoethyl)-hexahydroisophthalate (VI, R=Br). —The cyano-ester (VI, 15 g.) was heated with hydrobromic acid (48%, 53 c.c.) in a sealed tube for 6 hours at 140-50° and after dilution with water the heavy oily layer was extracted with ether and washed with sodium bisulphite solution. The dark oil (6·5 g.) from ether, after drying in *vacuo*, was treated with phosphorus pentabromide (20 g.) and left overnight, when a nearly complete solution resulted. After addition of absolute alcohol (50 c.c.) the mixture was allowed to stand for some time and finally heated on the steam-bath for 3 hours. On working up in the usual way, two fractions were collected. The first fraction (2 g.) had b.p. 133-38°/3·5 mm. and the second at 156-60°/3·5 mm. (2·5 g.)

The lower boiling fraction gave a very weak test for halogens and the nature of the product is still under investigation. The second fraction was the required bromo-ester (VII, R=Br). (Found : Br, 23·5. $C_{15}H_{23}O_4Br$ requires Br, 22·8 per cent).

Ethyl (1-Methyl-2 : 4-dicarbethoxy-cyclohexan)-1-propionate.— The bromo-ester (VII, R=Br; 2·5 g.) was treated with an aqueous alcoholic solution of potassium cyanide (1·5 g.) in presence of a little sodium iodide. The product after refluxing for 15 hours, was isolated in the usual way. Its ethereal solution was dried and directly esterified with alcohol (40 c.c.) and sulphuric acid (d 1·84, 8 c.c.) and two fractions isolated. The fraction (1 g.)

(b.p. 165-78°/1 mm.) was redistilled at 170-75°/2 mm. (lit. 170°/2 mm.). The quantity (o·5 g.) was, however, too small to permit further purification. (Found : C, 62·3 ; H, 8·2. $C_{18}H_{30}O_6$ requires C, 63·1 ; H, 8.7 per cent).

Further work is in progress.

My grateful thanks are due to Prof. P. C. Mitter for his valuable suggestions, kind encouragement and interest during the course of this investigation.

VAPOUR PRESSURES OF AQUEOUS SOLUTIONS.

BY G. S. KASBEKAR.

A new method has been devised to determine the vapour pressure of liquids and
solutions. Compared to other methods this method has been found to be simple, rapid
and to yield accurate and reproducible results. Observed values of vapour pressures of
aqueous solutions of $ZnCl_2$, $Ca(CNS)_2$, $Zn(CNS)_2$ and H_3PO_4 are recorded. From thermo-
dynamical considerations osmotic pressures of these solutions have been calculated.
Experimental results suggest a strong affinity between water and these salts which is in
agreement with the properties of these substances.
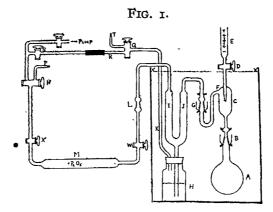
In connection with certain work which is in progress in this laboratory,
owing to lack of data in literature it was found necessary to determine the
vapour pressures of aqueous solutions of zinc chloride, calcium thiocyanate,
zinc thiocyanate and phosphoric acid. Among numerous methods deve-
loped for its accurate measurement, the 'dynamic' methods are more
tedious than the 'static' and demand an extremely careful manipulation.
Although the results obtained by the dynamic method are considered more
trustworthy, the static methods have been employed with great success.
After reviewing the works of Dieterici (*Wied. Ann.*, 1893, **80**, 47), Smits
(*Z. physikal. Chem.*, 1902, **39**, 385), Tower (*J. Amer. Chem. Soc.*, 1908, **30**,
1219), Wood (*Trans. Faraday Soc.*, 1915, **11**, 29), and Perman and Saunders
(*ibid.*, 1923, **19**, 112), it seemed possible to devise an alternative method,
which could be simple, rapid and yet reasonably accurate. The method
finally adopted is described in the following section.

EXPERIMENTAL.

All reagents employed in this investigation were analytical reagents
(certified B. D. H.). Solutions of various concentrations of the salts were
prepared by weight dilution from saturated solutions carefully filtered
through a sintered glass funnel. Syrupy phosphoric acid was used for
preparing solutions of that acid. The strength of the solution was deter-
mined by the estimation of both the components of the salt and only those
solutions were employed where the concentrations as determined by the
estimation of both the ions agreed within 0·2%. Zinc was estimated with
potassium ferrocyanide using methyl red as an adsorption indicator
(Tananaew and Georgofini, *Z. anal. Chem.*, 1936, **107**, 92). Potassium
palmitate method (Hamer, *J. Soc. Chem. Ind.*, 1935, **54**, 205) was employed

2

to estimate calcium. Chlorides were estimated with silver nitrate by the simplified potentiometric method (Callan and Horrobin, *ibid.*, 1921, **47**, 329) and the thiocyanates by the use of the same reagent but with ferric alum as an indicator. Wilkie's method (*ibid.*, 1909, **28**, 68) was adopted to estimate phosphoric acid.

Vapour pressures of these solutions were measured in a specially constructed apparatus (Fig. 1). A flask A (200 c.c.) was connected by a mercury sealed ground glass joint B to the bulb C, the top of which was sealed to a 10 c.c. burette E with a glass stop-cock D, while a side-tube led through another mercury sealed joint G to the mercury manometer IJ. Both the joints B and G were fitted with steel springs to keep them tight. The manometer was made of a wide tubing ($d = 1$ cm.) to minimise meniscus errors in reading and its lower end passed through a well fitting rubber stopper into a glass bottle H serving as a mercury reservoir. The reservoir was connected through K to the vacuum system. The limb I of the manometer was connected to a phosphoric pentoxide tube M through a ground glass joint L and a tap W. The other end of the P_2O_5 tube was connected to the vacuum system. All the ground joints and taps were greased with '.apiezon ' grease.

FIG. 1.

The apparatus could be separated into three parts R N M L, permanantly attached to the vacuum pump, Q H L G which carried the manometer, and E C B A which contained the solution under investigation. The piece E C B A was the only one which required to be cleansed and dried before each determination.

The apparatus was assembled together and immersed in the thermostat as shown in Fig. 1 with water upto the line XX'. A drop of mercury was introduced into the bore of the stop-cock D to remove air from there. 10 C.c. of the solution were placed in the burette E.

The interior of the apparatus was evacuated until a hard metallic sound of the pump indicated a good vacuum inside it. With tap W closed, Q was opened to air through T to let sufficient mercury rise into the manometer IJ. By the use of a travelling microscope the level in the two limbs was ascertained to be the same. The apparatus was left undisturbed for a couple of hours when no alteration in the two levels showed a good vacuum inside the apparatus. Now D is opened to let in about 7 c.c. of the solution into A. This causes a shift in the levels of mercury in the two limbs of the manometer. Readings of both the levels are taken at regular intervals until they show no change. The difference between the two levels gives the vapour pressure of the solution.

By appropriate manipulation mercury is withdrawn from the manometer into the reservoir and the tap W is kept open for 1 minute to connect the solution in A to the evacuating system. This causes the solution to ' boil ' and ensures the escape of any dissolved gases from it. Mercury is reintroduced into the manometer and the evacuation from the limb I continued until a good vacuum is obtained above the mercury level in it. The difference in the two levels was again noted. This second reading is inveriably lower than the first one and accounts for any dissolved gas in the solution. The process of ' boiling ' is repeated and a third reading is taken. The second and the third observations are usually found to be identical. If they differ from each other another reading is similarly taken. At the end of the experiment the solution in A was analysed to determine its strength.

By this method vapour- pressures of various different solutions and liquids (of which the vapour pressures are accurately known) were determined. Table I records the results of such measurements and it shows a satisfactory agreement between the observed and the ' standard ' values.

TABLE I.

Substance.	Temp.	Vapour pressure.	
		Int. Crit. Tables.	Author.
Water	25·0°	23·50 mm.	23·55 mm.
Water	26·0°	24·987	25·10
38 % H_2SO_4	25·0°	14·50	14·57
55 % H_2SO_4	25·0°	6·15	6·18

This agreement justified the final adoption of this method for measuring the vapour pressures of liquids and solutions.

Evacuation was done with the aid of a vacuum oil pump with an electric motor and a pressure of 0·02 mm. was recorded by Pirani gauge when evacuation was considered to be complete. All the experiments were carried out in a water thermostat electrically heated and regulated at 25 ± 0·02°.

Vapour pressures of the three salts and of phosphoric acid are recorded in Tables II-V.

TABLE II.

Zinc chloride at 25°.

% by wt.	Concentration. Molality. m.	Vapour pressure (mm. of Hg.).	Osmotic pressure (atmos.).
21·05	1·965	20·75	171·7
42·42	5·405	16·45	500·0
55·01	8·973	11·00	1081·0
57·62	9·977	9·70	1277·0
60·00*	11·01	8·10	1556·0
62·81	12·40	7·15	1760·0
65·00*	13·62	5·00	2330·0
67·51	15·25	4·20	2626·0
70·00*	17·12	2·90	3252·0
73·03	19·89	1·30	4650·0
75·02	22·04	0·60	5560·0

* Menezies and Boving (8th *Int. Con. App. Chem. Rep.*, 1912).

TABLE III.

Calcium thiocyanate at 25°.

% by wt.	Concentration. Molality.	Vapour pressure.	Osmotic pressure.
8·69	0·6092	22·80	14·63
19·52	1·552	20·70	174·6
31·32	2·919	17·30	430·3
40·48	4·355	12·20	937·0
51·13	6·699	7·70	1617·3
57·98	9·835	3·40	2873·0

TABLE IV.

Zinc thiocyanate at 25°.

% by wt.	Concentration. Molality.	Vapour pressure.	Osmotic Pressure.
8·778	0·5302	22·80	41·44
19·07	1·132	22·20	99·87
26·56	1·993	21·75	.105·7
34·42	2·894	20·25	205·9
38·70	3·477	19·45	262·6
42·19	4·021	18·80	310·1
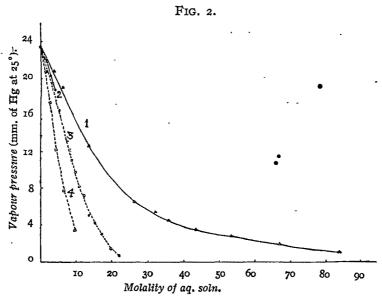
TABLE V.

Phosphoric Acid at 25°.

Concentration.		Vapour pressure.	Osmotic pressure.
% by wt.	Molality.		
12·92	1·513	22·0	89·8
28·38	4·041	20·8	166·6
38·81	6·469	19·0	291·8
57·49	13·79	12·65	873·1
72·12	26·39	6·45	1917·0
75·93	32·18	5·30	2231·0
77·91	35·97	4·40	2537·0
80·83	43·00	3·40	2976·0
83·85	52·65	2·70	3381·0
86·80	67·05	1·80	4101·0
89·15	83·77	0·90	5335·0

DISCUSSION.

Relation between vapour pressure and concentration is shown graphically in Fig. 2, and it is evident from the nature of the curves that the lowering in vapour pressure is not proportional to the concentration of the solute. With zinc thiocyanate, however, the lowering in the vapour pressure seems to be almost proportional to the concentration of the salt in solution.

FIG. 2.

Curves 1-4 refer respectively to H_3PO_4, $Zn(CNS)_2$, $ZnCl_2$ and $Ca(CNS)_2$.

From a knowledge of the vapour pressures of these solutions their osmotic pressures can be calculated. Porter (*Proc. Roy. Soc.*, 1908, **79**, 519; **80**, 457) evolved an equation relating vapour pressure to osmotic pressure of a solution from purely thermodynamic considerations. The form of equation given by Porter has been integrated and rearranged as follows by Wood (*loc. cit.*).

$$Ps(\mathbf{1} - \infty P/2) = RT \log_e \frac{\pi_0}{\pi_\pi} = C(\pi_0 - \pi_\pi) + (b - s)(\pi_0 - \pi_\pi)$$

where,

$P =$ the osmotic pressure of the solution when it is under its own pressure.

$s =$ shrinkage in volume of solution when 1 g. of solvent is removed from an infinite volume.

$\infty =$ compressibility of water at $T°$ absolute.

$\pi_0 =$ vapour pressure of water under its own v.p.

$\pi_\pi =$ vapour pressure of solution under its own v.p.

$C =$ concentration of solution.

$b =$ constant in Callender's gas equation.

R and T have their usual significance.

In applying the equation it is permissible to drop the last term since both b and s are nearly equal to unity. Shrinkage s is calculated from density data from an expression given by Callendar (*Proc. Roy. Soc.*, 1908, **A, 80**, 466).

With the aid of this equation, osmotic pressures of all the solutions have been calculated and it is found that excepting in the case of zinc thiocyanate, the calculated values of the osmotic pressure are of the order of a few thousand of atmospheres. What exactly such high values of osmotic pressure mean is difficult to conceive but it is clear that if such solutions were separated by semipermeable membranes from the pure solvent, enormously high pressures will have to be applied to the solution to prevent osmosis. The figures in other words indicate the strong affinity which zinc chloride, calcium thiocyanate and phosphoric acid have towards water, an indication which is in agreement with other properties of these substances.

DEPARTMENT OF CHEMISTRY,
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PHYSICAL CHEMISTRY OF RESIN SOLUTIONS. PART III. VISCOSITY OF SHELLAC SOLUTIONS IN MIXED SOLVENTS.

By Santi Ranjan Palit.

The viscosity of shellac dissolved in a solvent mixture composed of two non-solvents, acetone and water has been studied over a wide range of concentration and temperature The viscosity-solvent composition curves show well-defined minimum at a definite ratio of water to acetone in the solvent mixture for shellac concentration of 25% and higher; the lower the temperature, the more sharp and well-defined are the minima. For lower concentrations of shellac below 20% the viscosity continually rises with increase in the proportion of water. This striking difference in properties in shellac solutions in aqueous acetone below and above 20% of shellac has also been noted in the case of some other properties, e.g., gelation capacity, temperature coefficient of relative viscosity, etc., for which either solvation or micelle formation has been suggested as explanation. The solvent power as determined by precipitation with an inert solvent like benzene, or by cooling, always shows a maximum at about 80% water content. Thus the idea that viscosity is a criterion of solvent power is shown to be of restricted validity.

Viscosity data for solutions in a mixture of solvents, where neither of the components alone can dissolve the substance but the mixture has good solvent power, are valuable from theoretical as well as technical points of view. It has been observed by the author (Palit, *J. Indian Chem. Soc.*, 1940, 17, 308) that resins show solubility in a mixture of two non-solvents. Thus shellac (pure resin) is soluble in a mixture composed of either acetone or methyl acetate as one component, and water or glycol as the other, though none of the above-mentioned solvents dissolves the pure dry resin. These systems are particularly suitable for viscosity studies in mixed solvents as they are generally free from many disturbing effects usually associated with substances like cellulose derivatives, proteins, etc. These solutions as shown by the author in a previous paper (Palit, *ibid.*, 1940, 17, 537) are non-colloidal, have comparatively low viscosities (at least 1000 times lower than cellulose esters of the same concentration), are amenable to experimentation at high concentrations (even up to 50% or more) and show fairly reproducible behaviour. The present paper deals with viscosity studies of such systems under varying conditions of concentrations and temperatures. An attempt has also been made to study the relationships between viscosity and solvent power. The latter being determined by the method of precipitation by the addition of a non-solvent or by lowering of temperature.

S. R. PALIT

E X P E R I M E N T A L.
'Apparatus and Method.

Dewaxed shellac, powered to 100 mesh and dried at 42° in vacuum for 4 hours, was stored in a vacuum desiccator and used as required. Each lot was finished within a few days as standing over sulphuric acid for any length of time might induce insolubility in the shellac. The solvents were of Merck's chemically pure quality, which were dried and purified by distillation by usual procedure.

Viscosity measurements were carried out in Hoeppler viscometer (industrial type) using appropriate balls (A and B), temperature being controlled by circulating water round the viscometer tube from a thermostat kept at ±0˙05°.

Solutions were prepared by weighing out shellac in stoppered conical flask and adding to it the necessary volumes of solvents from appropriate burettes and microburettes. To hasten solution, the flask was placed in a water-bath at about 40°, and after the whole had dissolved, which usually took about 5 minutes or less, the solution was quickly filtered through a No. 1 or No. 2 fritted glass filter to free it from the traces of extraneous insoluble impurities (less than 0˙1%). The viscosity does not depend on the method of preparation or time. In fact, it was observed that even on gelation of the solution on keeping at lower temperature and remelting it, the viscosity assumed the same value at temperatures higher than the gelation temperature by 5° or more. Similarly, the time factor was also tested.
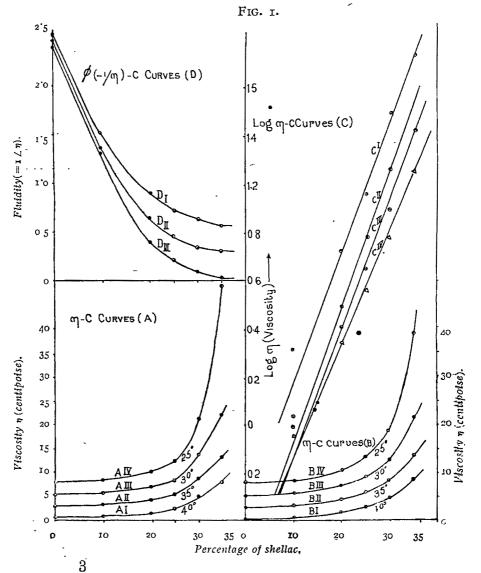
Solvent power as determined by precipitation with a non-solvent could not be measured by using the inert petroleum fraction such as heptane as advocated by Davidson and Reid (*Ind. Eng. Chem.*, 1927, **19**, 977) due to its limited miscibility with the shellac solutions in question. Dry benzene or toluene was used which was added drop by drop to a known weight of shellac solution kept in a test tube immersed in a thermostat at 25° or 30°, until the first appearance of haziness could be observed.

Precipitation temperatures were measured by immersing a small quantity (5 c.c.) of the solution contained in test tubes in water kept inside a thermoflask whose temperature was gradually lowered in steps of a quarter of a degree every five or ten minutes. The temperature at which opalescence could be observed in ten minutes was taken to be the precipitation temperature. Gelation temperature was observed by the same procedure ; the point at which the liquid did not flow on inversion of the test tube was taken as the gelation temperature.

The method of expressing concentration is as follows. A 30% shellac solution in aqueous acetone containing 10% water means that the solution contains 30 g. of shellac to 70 g. of solvent, the latter being composed of 10% water and 90% acetone by weight.

Viscosity and Concentration.

Viscosity is influenced by various factors including concentration, temperature and composition of the solvent.   The variation of viscosity with concentration of shellac is shown in Fig. 1 (curves AI, II, III and IV and BI, II, III, IV).   It will be observed that like all lyophilic compounds, *e.g.* polystyrenes, rubber, cellulose esters, etc., the relationship is not a linear one ; the viscosity rises slowly at first and then rapidly afterwards with concentration.   From the graph it may be observed that the rapid rise takes place for concentrations higher than 20% of shellac.

FIG. 1.

Percentage of shellac.

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No formula is sufficient to represent the curves over the whole range of concentration. Einstein's formula is evidently inapplicable. If according to Bingham ("Viscosity and Plasticity," p. 202), fluidity, $\phi (= 1/\eta)$ is plotted against concentration, straight lines are not obtained but like nitrocellulose solutions (Bingham, *loc. cit.*, p. 280) a definite asymptotic curvature is observed as shown by a few typical curves in Fig. 1 (D curves). Arrhenius' formula, log. $\eta/\eta_0 = C \log A$ (Hatschek, "Viscosity of Liquids," 1929, p. 114) is to some extent applicable as shown by the log $\eta - C$ curves in Fig. 1 (CI, II, etc.). It should be pointed out that though the points are approximately linear for 20% or higher concentrations, for lower concentrations, *e.g.* 10% or so, the formula is totally inadequate and the points representing these concentrations are widely out of the straight lines obtained by joining the corresponding other points.

Viscosity and Composition of Solvents.

With the same percentage weight of the solute, if the ratio of water to acetone in the solvent mixture is changed, the viscosity of the solution is profoundly influenced. Some typical curves are shown for shellac concentrations of 10, 20, 25, 30 and 35% in the graphs (Fig. 2—6) and relevant
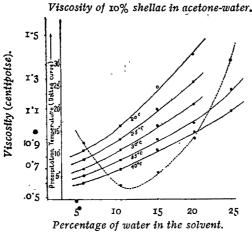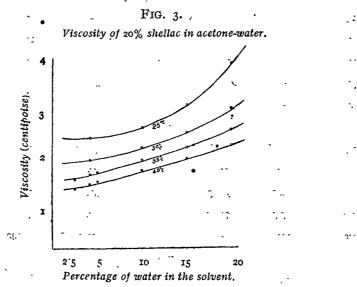
FIG. 2.
Viscosity of 10% shellac in acetone-water.

Percentage of water in the solvent.

data presented in Table I. It will be observed from the graphs that all the curves containing 30 or 35% shellac show minima at a concentration of water slightly greater than 10%. For 25% shellac the curves for lower temperatures (20° and 25°) show definite minima whereas the curves at 35° and 40° only tend to show the minima as a slight sag in the curve at that composition. This minimum viscosity occurs unlike the other curves on the initial portion of the curves at a concentration of less than 10% of water,

which is due to the fact that the gelation temperatures of these solutions containing small quantities of water are close to the temperature of measurement and so the initial portions have high viscosities and on increase of water concentration the gels are gradually broken down to mobile fluids.

FIG. 3.

Viscosity of 20% shellac in acetone-water.

For 20% shellac concentration, the minima are absent but perhaps a small sag is still noticeable in the curves for lower temperatures. For 10% shellac concentration, no trace of minima is noticeable but the viscosity continually rises with increase in water content of the solvent. To sum up, the minima appear in the viscosity-solvent composition curves for concentrations of 25% or more of shellac, more prominently the lower the temperature but for lower concentrations (e.g. 10% shellac) no minima exist, the general shape of the curves being the same as the viscosity diagram of the pure solvent mixture.

TABLE I.

Viscosity of shellac solutions in aqueous acetone.
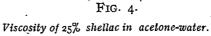
% Water in acetone.	Ppt. or gel. temp.	Viscosity (centipoise) at				
		20°.	25°.	30°.	35°.	40°.
		Shellac=10%.				
5·0	12·5	0·824	0·761	0·702	0·652	0·610
10·0	3·0	0·987	0·899	0·827	0·757	0·696
15·0	7·0	1·241	1·099	0·988	0·897	0·825
20·0	12·5	1·454	1·273	1·127	1·011	0·943
25·0	30·5	—	—	—	1·222	1·052

TABLE I (contd.).

% Water in acetone.	Ppt. or gel. temp.	Viscocity (centipoise) at				
		20°.	25°.	30°.	35°.	40°.
			Shellac=20%.			
2·5	—	—	—	—	1·512	1·316
5·0	—	—	2·52	1·991	1·671	1·478
10·0	—	3·22	2·641	2·226	1·941	1·716
15·0	—	—	3·161	2·565	2·218	1·996
20·0	—	—	4·069	3·077	2·617	2·278
			Shellac=25%.			
2·5	20·0°	gel	6·080	3·622	2·770	2·319
5·0	12·5	7·288	4·734	3·485	2·848	2·417
10·0	2·75	7·015	4·864	3·841	3·170	2·707
15·0	5·5	7·829	6·092	4·499	3·669	3·098
20·0	10·0	—	—	5·257	4·142	3·458
			Shellac=30%.			
2·5	22·0	gel	gel	10·2	6·36	4·83
5·0	17·5	53·5	13·9	8·77	6·27	4·88
10·0	12·0	19·82	11·0	7·81	5·92	4·79
15·0	10·5	19·91	11·55	7·83	6·06	4·89
20·0	14·5	34·6	16·2	10·1	7·34	5·77
25·0	24·0	—	—	16·4	9·80	7·21
			Shellac=35%.			
2·5	23·25	—	565·0	23·04	12·16	8·27
5·0	20·0	—	41·31	17·19	10·73	7·87
10·0	16·25	—	15·5	9·91	7·16	5·61
15·0	17·25	—	31·61	16·82	11·32	8·59
20·0	21·25	—	60·5	25·83	15·47	11·11

Viscosity and Solvent Power.

The precipitation temperature-solvent composition curves show minima at the compositions corresponding to the minima in the viscosity curves. Even where the viscosity curves show no minima but tend to rise continually, the precipitation temperature curves exhibit the minima as usual.

This is shown in the dotted curves in Figs. 2—6, where the temperature of precipitation or gelation which is a measure of solvent power in the reciprocal sense, has been plotted. Also the dilution ratio (*i.e.* the volume of benzene or toluene necessary to be added to just precipitate shellac from one gram of solution), which may be regarded as constituting a direct measure of solvent power (though such an assumption is not free from objection as can be inferred from the work of Davidson and Reid, *loc. cit.*) always tends to show maxima at the composition corresponding to the minima in the viscosity curves. The following figures for 10%, 20% and 30% shellac solutions are, however, sufficient to establish the general trend as mentioned above.

FIG. 4.

Viscosity of 25% shellac in acetone-water.

Perecntage of water in the solvent.
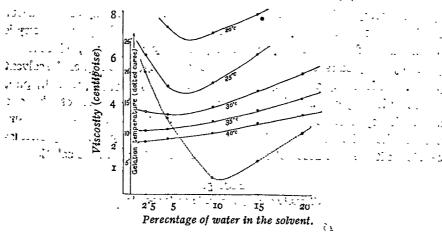
TABLE II.

Dilution ratio

Percentage of shellac in solution.	Percentage of water in the solvent mixture.					
	2·5%.	5%.	10%.	15%.	20%.	25%.
10%	—	0·79	0·57	1·47*	0·22	—
25%	0·69	0·81	0·53	0·39	0·19	—
30%	0·58	0·64	0·67	0·31	0·18	0·09

To sum up, therefore, the solvent power as determined by both the methods always shows maxima at a definite ratio of water to acetone in the

* Shellac could not be precipitated even by this maximum amount of benzene miscible with the solution.

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solvent mixture regardless of the concentration of the solute or of the nature of the viscosity curves.

DISCUSSION.

It is generally believed as a result of the viscometric studies of Gibson and McCall (*J. Soc. Chem. Ind.*, 1920, **39**, 172T), Masson and McCall (*J. Chem. Soc.*, 1920, **117**, 819),Highfield (*Trans. Faraday Soc.*, 1926, **22**, 57), McBain, Harvey and Smith (*J. Phys. Chem.*, 1926, **30**, 212), on nitrocellulose solution and of Barr and Bircumshaw (*Trans. Faraday Soc.*, 1921, **16**, 99), Mardles (*J. Soc. Chem. Ind.*, 1923, **42**, 207T) and Sheppard, Carver and Houck (*Coll. Sym. Mon.*, 1927, **5**, 243), etc., on cellulose acetate solutions that some optimum composition exists for solvent mixtures composed either of two non-solvents or of one solvent and another latent solvent. At this optimum composition the solvent power as determined by any of the various empirical methods widely used in the nitrocellulose lacquer industry is maximum and the viscosity is correspondingly a minimum, since it is a generally accepted fact that the lower the viscosity, the higher the solvent power. This is expressed by Durran (" Solvents," 1933, 3rd Ed., p.2), as ' The viscosity of a solution of cellulose nitrate in mixtures of ether and alcohol is dependent on the ratio of ether to alcohol and reaches a minimum at a definite ratio. This ratio is a characteristic property of the particular cellulose nitrate but does not depend on the amount of it in the solution."

FIG. 5.
Viscosity of 30% shellac in acetone-water

Percentage of water in the solvent.
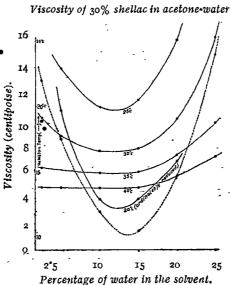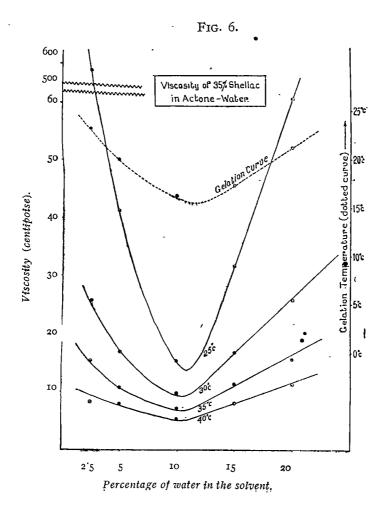
The present work, however, demonstrates that the existence of minima n the viscosity-solvent composition curve is not a general behaviour but occurs only when the concentration of shellac exceeds certain value (about 20% of shellac). The fact that the nature of the curve changes below and above a certain concentration is of greater significance than what only appears from the above diagrams and a comparison of the properties of the system below and above this concentration offers certain other singularities
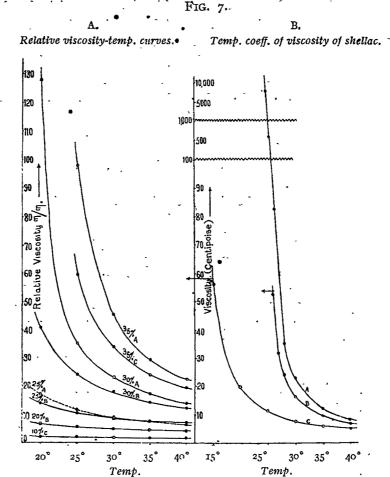
It has been observed that all solutions above this minimum concentration (20-25%) form transparent, clear, thermoreversible gels on cooling whereas on cooling a shellac solution, which is below this minimum concentration, the solid separates out as flakes or curd with scarcely any tendency towards forming a transparent jelly. From a concentration of about 20%

FIG. 6.

Percentage of water in the solvent.

and upwards, the solution on cooling becomes somewhat hazy due to the separation of a number of flakes and then it forms a clear gel in which the flakes may be seen embedded. The amount of flakes separating during gelation gradually decreases as the concentration increases until at just above 25% shellac concentration, gelation absolutely free from precipitation takes place. This gradual transition from precipitation through curd-formation to gelation, perhaps shows that an increase of concentration brings about some fundamental change in the nature of a closer relationship between the solvent and the solute.

Of course, this may mean simply that just like other lyophiles, e.g. gelatine, cellulose acetate, etc., for which a minimum concentration of the colloid is necessary for gelation as observed by various workers of which a summary is given by Mardles (*Trans. Faraday Soc.*, 1923, **19**, 118), this minimum gelation concentration is unusually high for the shellac system and happens to be at 20-25% of shellac. Though this is mainly correct, the already mentioned peculiarities in the viscosity-solvent composition curve and viscosity-concentration curve are also worthy of notice. Besides, though Arrhenius' equation is approximately valid above this concentration, it totally ceases to be so below a concentration of 20%.

A comparative study of the temperature coefficient of relative viscosity, as has been done in Fig. 7 where η/η_0 has been plotted against temperature, η and η_0 signifying the viscosity of the solution and the solvent respectively at the same temperature, reveals some interesting features. It is clear from the almost horizontal course of the graph that upto the minimum concentration referred to, the temperature coefficient of the solution is slightly higher than that of the pure solvent, whereas for higher concentration (say 25%, 30% or higher) the relative viscosity falls steeply with temperature. The latter behaviour is characteristic of all lyophilic substances (Hatschek, *loc. cit.*, p. 114), whereas for lyophobic substances, relative viscosity maintains about a constant value over a wide range of temperature. The conclusion seems irresistible that over a small range of concentration of the solute, it changes from lyophobic to lyophilic nature, and perhaps this transition to the lyophilic state is responsible for the gel-forming property of the solution. The high temperature coefficient of viscosity particularly near about gelation point is also worthy of notice. The viscosity amounts to a few poises only at three or four degrees higher than the gelation point and within this small range of temperature the viscosity rises to infinity (*i.e* the solution gels). This is shown graphically for a few typical solutions in Fig. 7.

FIG. 7.

A.   B.

Relative viscosity-temp. curves.   *Temp. coeff. of viscosity of shellac.*

All the above observations may also be explained from considerations of the colloid nature of such solutions, though it has been previously shown by the author (*loc. cit.*) and also by Houwink " Nature und Kunstharzen", 1934, p. 206) from viscometric studies that at least in dilute solutions shellac and most other natural resins exist in the truly dissolved state. It may be that over the small range of concentration through which gelation properties appear, micelles are being formed by the reversible association of resin molecules, and this may be responsible for the latter behaviour of the system. The existence of micellar aggregates in concentrated solutions to which is to be primarily attributed the gelation capacity of the system, is gradually weakened by the initial addition of water, perhaps due to adsorption of water on the smaller units to form a protective layer, with consequent decrease of of viscosity and increase of solvent power. The final increase of viscosity

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with further addition of water may, on this view, be explained as due to increased micelle formation as a result of decrease in solubility of the resin by the addition of a non-solvent water. •The parallelism of this hypothesis with the behaviour of soap solutions is only too apparent, since the existence of a critical micellar concentration for the aqueous soap solution have recently been proved (Hartley, *J. Amer. Chem. Soc.*, 1936, **58**, 2347), beyond dispute. The parallelism with soap further consists in that like shellac system in question, alcoholic solutions of soap are molecularly disperse at least in dilute solutions, though soapy solutions in organic solvents are well known (*vide*, Lederer, " Kolloidchemie der Seifen," pp. 78, 229), to produce very stiff jellies on cooling.

It is easy to see from the literature why previous workers invariably obtained a minimum in the viscosity-solvent composition curves. They have always directed their work to such concentrations of the solute as are well above the minimum gelation concentration, which is very low (less than 0.5%) for substances like cellulose esters, rubber, etc., which have hitherto been the main objects of investigation.

Since, as already pointed out, the solvent power-solvent composition curves always exhibit maxima even for low concentrations of shellac (10%) where the viscosity continually increases with increase in the concentration of water, the solvent power is in no way parallel or related to the viscosity of the solution. A solvent containing about 10 to 15% water may, in this case, be justly regarded a better solvent than one containing, say 5% water, because from the latter the dissolved shellac is more easily precipitated by a lowering of temperature or by the addition of a non-solvent; but the viscosity of the former solution is certainly much higher than the latter (Fig. 4). We may, therefore, qualify the prevalent general belief first expressed by Schwartz and upheld by McBain and co-workers (*loc. cit.*), that " the best solvents yield solution of lowest apparent viscosities", by adding that this is true only above the minimum gelation concentration but may sometimes totally fail below this minimum concentration.

CHEMICAL REACTIVITY AND LIGHT ABSORPTION. PART IV.

By N. R. Dhar, A. K. Bhattacharya and S. P. Agarwal.

Total absorption of light by a mixture of the reacting substances has been observed to be greater than the absorption of each substance taken separately in reactions studied in the present paper. The increase in light absorption in each case varies with the concentration of the reducing agent. The dark reaction velocity also decreases with the decrease of concentration of the reducing agent. The chemical reactivity and the increase in the light absorption by a mixture are almost equally affected by a change in concentration of the reducing agent. The increased light absorption appears to be due to the activation of molecules in the presence of the molecules of the sensitising agents. The activation of the molecules is associated with loosening of the binding forces and the consequent increased light absorption.

In previous publications (*J. Indian Chem. Soc.*, 1934, **11**, 33, 311, 629; *Indian J. Phys.*, 1936, **10**, 43) it has been shown that the introduction of a reactive chemical substance in a light absorbing substance increases its power of absorbing light. The increased absorption appears to be due to the activation of the molecules of the absorbing substance. It has also been shown that in the reaction between sodium formate and iodine an increase in the concentration of one of the reacting components leads to an increase in light absorption by a mixture of sodium formate and iodine. From our experimental observations it appears that the heat of reaction and increased light absorption go hand in hand.

In this paper the influence of concentration of one of the reacting components on the chemical reactivity and light absorption in the case of several reactions has been investigated.

EXPERIMENTAL.

For photographing the absorption spectra, two spectrographs (Adam Hilger, Quartz Spectrograph, Types E_3 and E_1) were used. In these experiments a copper arc worked with 220 volts and 4·5 amperes was utilised as a source of light. The reaction vessel was of quartz with internal dimensions 13 cm. × 3 cm. × 5 cm. Results have been recorded below.

Oxalic Acid and Chlorine.—Both the reacting substances being photosensitive, the reaction is very fast in absence ot hydrochloric acid, and its velocity is difficult to measure. Hence hydrochloric acid was added to retard the reaction. The photographs and the following results show that

the greater the concentration of oxalic acid and hence the greater the velocity, the greater is the absorption of light by the mixture (Table I).

TABLE I.			TABLE II.	
Oxalic acid.	Increase in light absorption by the mixture	k_1 (unimol. vel. coeff., in region $\lambda = 3125$Å.	Ferrous sulphate	Increase in light absorption by the mixture.
$N/10$	324Å	0·1209	4%	162Å
$N/20$	254Å	0·067	2%	92Å

Ferrous Sulphate and Iodine.—In this reaction also an aqueous solution of iodine was used. Both the components are light sensitive (Table II).

Sodium Tartrate and Iodine.—Increased light absorption by the mixture is observed with increase in the concentration of the tartrate solution.

Sodium Formate and Iodine.—Dhar and Bhargava (*J. Phys. Chem.*, 1935, **39**, 1231) investigated the light absorption by mixture of sodium formate and iodine dissolved in potassium iodide. In this paper, the results obtained by using aqueous solutions of iodine are recorded (Table III).

TABLE III.			TABLE IV.	
Sodium formate.	Increased light absorption by the mixture	k_1 (unimol. vel. coeff. in the dark).	Hydroxylamine hydrochloride	Total absorption from wave-length.
$N/2$	162Å	0·246	$N/2$	3028Å
$N/4$	92Å	0·124	$N/4$	2905Å
			$N/20$	2823Å

Hydroxylamine Hydrochloride and Iodine.—In this reaction as well as in the reaction with hydrazine sulphate hydrochloric acid has to be added, as the reaction was too fast to be measured in absence of the acid (Tables IV and V).

TABLE V.		TABLE VI.	
Hydrazine sulphate and iodine. (HCl added.)		*Ferrous ammonium sulphate and silver nitrate.*	
Hydrazine sulphate	Increased light absorption by the mixture.	Ferrous ammonium sulphate.	Increase in light absorption by the mixture.
$N/50$	208Å	0·4%	46Å
$N/100$	185Å	0·2%	25Å
$N/500$	162Å		

Acetone and Iodine.—In this reaction also, the greater the concentration of acetone, the greater is the light absorption by the mixture.

It was shown by Dawson and others (*J. Chem. Soc*, 1909, **95**, 1860 ; 1913, **103**, 2135) that the reaction between acetone and iodine is catalysed by hydrogen ions. The effect of the catalyst is only to increase the velocity

of enolisation of acetone, which takes place according to the following scheme :—

$$H_3C-C-CH_3 \rightleftharpoons H_2=C-CH_3$$
$$\quad\quad \| \quad\quad\quad\quad\quad\quad |$$
$$\quad\quad O \quad\quad\quad\quad\quad\quad OH$$

This increase in velocity is directly proportional to the concentration of hydrogen ions. We have photographed the absorption spectra of the mixture of acetone and iodine, using a wide range of concentration of hydrochloric acid, viz., from 12·0 N to 0·17 N. The results are recorded on Plate I. The spectra shows a regular decrease in absorption as the concentration of hydrochloric acid decreases.

These results lend strong evidence in support of the view that the increase in light absorption is the direct result of the increased chemical reactivity of the molecules.

Potassium Permanganate and Hydrochloric Acid.—The photograph brings out that in this reaction, the greater the concentration of hydrochloric acid the greater is the increase in light absorption by the mixture.

From the photographs it is also evident that complete absorption by the reacting-mixture begins from a longer wave-length than that by the reacting components and that the increase in the concentration of the reducing agent leads to more light absorption by the mixture.

Our results further show that with the decrease in concentration of the reducing agent, the velocity of the reactions concerned and the chemical reactivity of the mixture diminishes as also the light absorption. The photographs also reveal that with a very dilute solution of the reducing agent, the mixture does not show any appreciably enhanced absorption and at these concentrations the velocity of the chemical reactions is also almost negligible.

These investigations on the influence of concentration on chemical reactivity and light absorption have further supported the observations of Dhar and Bhattacharya (*J. Indian Chem. Soc.*, 1934, **11**, 33) that several reactions show marked acceleration by infra-red radiations of wave-lengths 7304 Å and 8500 Å because the presence of the reducing agent markedly sensitises the decomposition of the other molecules.

These observations showing that the chemical reactivity between the substances is accompanied by increased light absorption, and this phenomenon of sensitised decomposition bring to a close the long controversy regarding the minimum frequency of radiations capable of initiating the chlorine-hydrogen reaction, because in presence of hydrogen the Cl-Cl

link, is considerably weakened and hence radiation of wave-lengths longer than 5000 Å, which are capable of atomising a chlorine molecule, can initiate the chemical change.

From our results with mixtures of hydrogen and chlorine, hydrogen and bromine vapour, methyl alcohol vapour and bromine vapour, ethyl alcohol vapour and bromine vapour etc., it is clear that the light absorption by a mixture of the reacting substances occurs over a wider region of the spectrum than in the case of absorptions by the ingredients considered separately. It is interesting to note, that there is no variation in the position of the absorption limit when the gases or vapours are passed through concentrated sulphuric acid or phosphorus pentoxide. In other words, desiccation considerably decreases the chemical reactivity and prevents the combination of hydrogen and chlorine or hydrogen and bromine in the visible region. Hydrogen sentitises the dissociation of chlorine and bromine molecules and makes them reactive in radiations of longer wave-lengths only in the presence of moisture. These observations support the important work of Baker who showed that intensive drying greatly reduces the reaction velocity of substances. Baker (*J. Chem. Soc.*, 1906, **89**, 1402) and Tamm (*Z. physikal. Chem.*, 1923, **105**, 356) showed that hydrogen and chlorine, dried over phosphorus pentoxide did not combine at all in visible light. Coehn and Jung (*Z. physikal. Chem.*, 1924, **110**, 705) found that there was no combination in the system where the pressure of water vapour was estimated to be 10 mm. of Hg., no reaction occurred even after 20 days' exposure to sunlight, but that the reaction took place rapidly when the pressure was 10^{-5} mm. Bodenstein and Dux had found that the variation of water vapour between 10 mm. and 10^{-3} mm. had no effect on reactions between hydrogen and chlorine and concluded that the non-reactivity of gases dried over phosphorus pentoxide might be due to some inhibition.

It can now be stated with a certain amount of definiteness that the appearance of a continuous absorpsion (non-quantised absorption) spectrum of a gas is always a case of photochemical dissociation taking place in the gas. Moreover, convergence limits in continuous absorption have up till now been observed only for those molecules in which the binding forces are appreciably weakened by light absorption.

It appears, therefore, that increase in light absorption by a molecule is associated with it increased reactivity and loosening of the binding forces. Conversely when a molecule becomes more reactive, it is likely to absorb light more markedly.

Victor Henri has reported that with an increase of temperature the limit of dissociation is shifted towards the higher wave-length side and that

the radiation corresponding to the region of predissociation causes photo-chemical reaction or chemical sensitisation of the molecules.

From the researches of Henri and others, it is clear that on increasing the temperature, the absorption limit is shifted and the molecules dissociate on illumination by radiations of longer wave-lengths. Thus with acetaldehyde, the absorption spectrum at the laboratory temperature consists of a large number of sharp bands with definite structure between $\lambda3484$ to $\lambda3050$. Near $\lambda3050$ the bands become blurred rapidly due to predissociation of the molecule and about 60 diffuse bands reaching up to $\lambda2823$ have been measured. Also there is superimposed on these diffuse bands, a broad continuous band starting at about $\lambda3080$ with a maximum at $\lambda2850$ and which subsequently falls off in intensity more and more on the ultraviolet side. If acetaldehyde vapour is heated to 200°, feeble diffuse bands appear between $\lambda3500$ and $\lambda3200$ with a strong continuous absorption reaching far into the ultraviolet. When acetaldehyde vapour is illuminated at the laboratory temperature, decomposition takes place into CO and CH_4, only when the wave length is $\lambda3002$ or shorter ; whilst at 200°, vapour can be photolysed by radiations of wave-length exceeding $\lambda3100$.

It appears, therefore, from these researches on photochemical decomposition and predissociation that the increase in the chemical reactivity of a substance by increase of temperature is associated with a shift in the position of the absorption bands specially in the ultraviolet region. Moreover, increased temperature of the molecule sensitises them towards their decomposition by longer wave-lengths. Hence the weakening of the binding forces of molecules and their consequent unstability are associated with shift of absorption bands and of the limit of continuous absorption by the molecules.

Just as an increase of temperature or light absorption weakens the binding forces of a molecule. the introduction of a chemical substance into an absorbing system may also loosen the binding forces of a molecule. For example, the presence of a reducing agent accelerates the decomposition of an oxidising molecule. Thus in presence of reducing agents like hydrogen, carbon monoxide, ferrous salts, nitrites, hydroxylamine, alcohols, accetone, organic acids and their salts, etc., the halogen molecules become reactive even in the dark as well as when exposed to radiations of wave-lengths longer than those necessary for their sensitised or photochemical dissociation, because the binding forces of the halogen molecules are considerably weakened due to the presence of the reducing agents.

It has been shown previously with numerous reactions taking place in solutions that the light absorption by a mixture of the reacting substances

is always greater than the absorption of the ingredients considered separately. The increase in absorption appears to be due to the activation of the molecules by the presence of the molecules of the other substances. The activation of the molecules is associated with the weakening of the binding forces and consequent increased light absorption.

The observations of Weigert and Kellermann (*Z. physikal. Chem.*, 1923, **107**, 1) on increased light absorption by a mixture of chlorine and hydrogen and the increased light absorption observed by J. C. Ghosh and collaborators (*J. Indian Chem. Soc.*, 1927, **4**, 353 ; 1928, **5**, 191, 569), with mixtures of organic substances and solutions of ferric and mercuric chlorides, and uranyl nitrate, can be interpreted on the viewpoint that the chemical reactivity of these various systems is associated with the weakening of the binding forces and increased light-absorption. Fajans and Karagunis (*Z. physikal. Chem.*, 1929, **B5**, 385) have shown that the light absorption by silver iodide containing adsorbed silver is appreciably greater than that of silver iodide containing adsorbed iodine or that of silver iodide alone. Moreover, it is well known that the silver halides containing adsorbed silver are more photosensitive and hence more liable to be decomposed in light than the silver halides containing an excess of the halogen. Similar results have been obtained with other silver halides. The presence of silver sensitises the photodecomposition of silver halides and weakens the binding forces between silver and the halogen atoms and causes increased light-absorption. From the above facts it can be concluded that the contact of one reacting substance with another weakens the binding forces of the molecules of reacting substances just as increase of temperature or light absorption loosens the binding forces. The close proximity or contact of another molecular species capable of chemically reacting with the first one, plays practically the same rôle as that of the physical agencies, *viz.* increase of temperature or light absorption.

From the numerous cases cited in this paper it seems clear to us that if there is possibility of the occurrence of a chemical change by mixing two or more substances, variation in the position of the absorption limit is likely to be observed in these cases. We are of opinion that the shift in the position of the absorption limit in the case of a mixture in comparison with those of the ingredients is likely to be a measure of the reactivity of a given mixture of two or more substances.
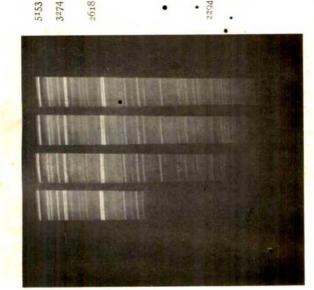
DHAR, BHATTCHARYA & AGARWAL

PLATE I.

Oxalic acid and chlorine.
Exposure = 5 secs.

5153 3274 2618 2294

1. Cu arc₈

2. N/150- chlorine.

3. (12 N-HCl + N/5-oxalic acid)+water.

4. (12 N-HCl + N/5-oxalic acid)+N/75-chlorine.

PLATE II.

Influence of the variation of conc. of HCl on the light absorption of acetone and iodine reaction,
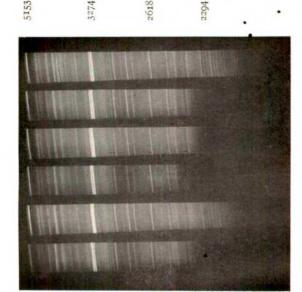Exposure = 10 sec.

5153 3274 2618 2294

1. Cu arc.
2. N/680-Iodine.
3. (1% acetone + 12N-HCl)+ H₂O.
4. (,, + 12N- ,,)+N/340-I₂.
5. (,, + 6N- ,,)+H₂O.
6. (,, + ,, ,,)+N/340-I₂
7. (,, + 3N- ,,)+H₂O.
8. (,, + ,, ,,)+N/340-I₂.
9. (,, + 1·7N- ,,)+H₂O·
10. (,, + ,, ,,)+N/340-I₂
11. (,, + 0·85N-,,)+H₂O.
12. (,, + ,, ,,)+N/340-I₂.
13. (,, + 0·17N-,,)+H₂O.
14. (,, + ,, ,,)+N/340-I₂.

PLATE III.

Sodium tartrate and iodine.

Exposure = 5 sec.

5153   3274   2618   2294
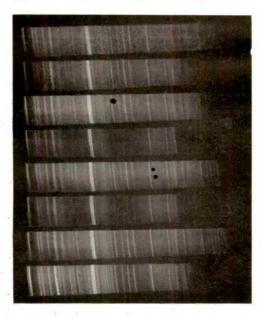
1. Cu arc.

2. $N/680$-I_2.

3. $N/4$-tartrate.

4. $N/2$-tartrate $+ N/340$-I_3.

5. $N/200$-tartrate.

6. $N/100$-tartrate $+$
   $N/340$-I_2.

PLATE IV.

Sodium formate and iodine.

Exposure = 3 sec.

5153   3274   2618   2294

1. Cu arc.

2. $N/680$-I_2.

3. $N/4$-formate.

4. $N/2$-formate $+ N/340$-I_2.

5. $N/8$-formate.

6. $N/4$-formate $+ N/340$-I_2.

7. $N/40$-formate.

8. $N/20$-formate $+ N/340$-I_2.

PLATE V.

Hydroxylamine hydrochloride and iodine.

Exposure = 3 sec.
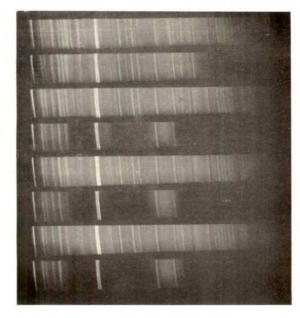
1. Cu arc.

2. $N/680$-I_2.

3. $N/4$-Hydroxylamine HCl.

4. $N/2$-   ,, $+ N/340$-I_2.

5. $N/8$-   ,,

6. $N/4$-   ,, $+ N/340$-I_2.

7. $N/40$-   ,,

8. $N/20$-   ,, $+ N/340$-I_2.

PLATE VI.

Hydrazine sulphate + iodine.

Exposure = 3 sec.

1. Cu arc.

2. $N/680$-I_2.

3. $N/100$-Hydrazine sulphate.

4. $N/50$-   ,, $+ N/340$-I_2.

5. $N/200$-   ,,

6. $N/100$,, $+$,,

7. $N/1000$-   ,,

8. $N/500$-   ,, $+$,,
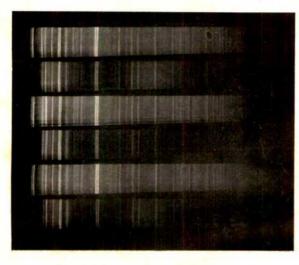
DHAR, BHATTACHARYA & AGARWAL

PLATE VII.

HCl + KMnO$_4$.

Exposure = 15 sec.

1. Cu arc.

2. $N/200$-KMnO$_4$.

3. 1·25-N-HCl

4. 2·5N-HCl + $N/10c$-KMnO$_4$.

5. $N/2$-HCl.

6. N-HCl + $N/100$-KMnO$_4$.

ESTIMATION OF ZINC IN SNAKE VENOMS BY· MICRO-QUINALDINATE METHOD.

BY PRIYADARANJAN RÂY

Percentage of zinc in various types of Indian snake venoms has been determined microchemically by means of sodium quinaldinate. It has been found that the zinc content varies from 0·56% in the case of *naja naja* cobra- venom to less than 0·02% for *Bungarus ceruleus* among the colubrides, and from 0·186% in the case of *Echis carinata* to 0·04% for *Russell's viper* among the viperides. In purified neurotoxin and haemolysin fractions of *Naja naja* cobra venom the zinc percentage is reduced to negligible amount. The results indicate that there is no relationship between the zinc content of the crude venom and its toxicity as was previously assumed by Delezenne. The sensitivity and the reliability of the quinaldinate method for the estimation of minute quantities of zinc in biological materials are thus clearly demonstrated.

Zinc has been found to be a constant constituent of all animal cells. Delezenne (*Ann. Inst. Pasteur*, 1919, **33**, 68) found that in the venom of serpents it is present to the extent of 0·31-0·56% in colubrides and 0·11-0·23% in viperides. According to his observations the proportion of zinc in the venom was found to vary inversely with the coagulating and proteolytic properties of the latter and directly with its nucleolytic and haemolytic activities.

The method of estimation adopted by Delezenne was the usual macro-method of precipitation as sulphide and ignition of the latter into oxide. As the estimation of small quantities of zinc by this macro-method is not likely to give very accurate results for the purpose of such comparisons between toxicity and zinc content of venoms, it was considered desirable to determine the zinc content of the venoms of certain Indian snakes by using a more dependable and refined method. Sodium quinaldinate was, therefore, selected as the most suitable reagent for the micro-chemical estimation of zinc in the venoms (Rây and Bose, *Mikrochemie*, 1935, **17**, 11).

It was also of interest to re-examine this problem, since Slotta and Fraenkel-Conrat (*Ber.*, 1938, **71**, 1078) in their work on the rattle snake (*Crotalus t. terrificus*) venom failed to detect the presence of zinc either in the crude venom or in the crystalline poison Crotoxin, isolated by them from the venom.

Seven different types of Indian snake venoms were analysed for zinc in our laboratory. Five of these are colubrides, such as cobra venoms—*Naja naja, Naja tripudian, Naja bungarus*, and the krait venoms—*Bungarus fasciatus* and *Bungarus ceruleus*. The other two are viperides—*viz.,*

Vipera russellii and *Echis carinata*. Zinc was found and estimated in all these crude venoms. The smallest percentage was found in *Bungarus ceruleus*. Though the maximum amount (0·56%) found in colubride venoms (*i.e. Naja naja*) corresponds closely with that obtained by Delezenne, there is, however, considerable discrepancy in the case of lower limit for both the colubrides and viperides (« 0·02% in *Bungarus ceruleus* and 0·04% in Russell's viper). Further, contrary to Delezenne's observations the toxicity in the two viperide venoms examined does not run parallel with the zinc content. The same holds good also with the colubride venoms.

The following table gives a comparative idea about the zinc content and the different aspects of activity of the venom.

TABLE I.

Venoms	Neurotoxic activity (same as the toxicity value).	Haemolytic activity.	Coagulating power.	Proteolytic power.	Zinc content (average).
Naja Bungarus	0·0033 mg.	Not determined.	...	+	0·04%
Naja naja	0·035	+++	...	+	0·554
Naja tripudian	0·030	+++	...	+	0·457
B. cerulens	0·0009	+++	...	+	0·02
B. fasciatus	0·370	++	...	+	0·0253
Echis carinata	0·0093	+	+	++	0·186
Vipera russellii	0·010	Less than Echis	++	+	0·04

(+ indicates moderate, ++ indicates high, +++ very high, ... indicates nil.)

The purified neurotoxin and haemolysin factors of *Naja naja* cobra venoms (Ghosh and De, *Indian J. Med. Res.*, 1938, 25, 779) were then examined for zinc content. The neurotoxin factors gave a rather low value (0·15 and 0·04% Zn), whereas haemolysin factor was practically free from it. It is quite likely that with further purification the neurotoxin factor will also be found to be free from zinc Obviously, zinc cannot be regarded as an essential constituent of the poison, present in the crude venom.

Method of Estimation.

Among the inorganic constituents of snake venom calcium, magnesium, sulphur and phosphorus were detected besides zinc. None of these elements interfere with the estimation of zinc as quinaldinate.

About 0·08-0·15 g. of the venom was treated with 1 c.c. of fuming nitric acid and 1 c.c. of perchloric acid in a small 50 c.c. beaker covered with a watch-glass. This was at first heated on the water-bath and then over an asbestos board. Thick white fumes of perchloric acid came out and the mixture was evaporated to dryness. The residue was again treated with a small quantity of perchloric and fuming nitric acid mixture, which was evaporated to dryness as before. The treatment with the acid mixture and evaporation were repeated for the third time when the residue obtained was perfectly white. All traces of perchloric acid were then removed by heating and the residue was moistened with a drop of concentrated hydrochloric acid. The excess of the latter was completely removed by heating the beaker on the water-bath. The dry mass was then treated with a drop of glacial acetic acid and dissolved in 1 or 2 c.c. of water by warming. The solution was filtered into a weighed micro-beaker and the filter paper washed with a small quantity of hot water. The volume of filtrate in the beaker was reduced by evaporation by placing the beaker in its holder on the water-bath. Zinc was then precipitated by sodium quinaldinate. The precipitate was filtered through an Emich's filter-stick, dried in Beneditti-Pichler's drying apparatus and then weighed on a micro-balance. (Râ   y and Bose, *loc. cit.*). Results of analysis are tabulated below.

TABLE II.

Venoms.	Wt. of venom.	ZnO_2.	Zn.	Analysed by	Toxicity value.
I. *Naja naja*	0·1414 g.	5·2466 mg.	0·5685%	T. C. Sarkar	
,,	0·1086	4·0280	0·5670	P. Rây	
II. ,,	0·1050	3·7580	0·5471	T. C. Sarkar	0·035 mg.
,,	0·0797	2·7580	0·5290	,,	
,,	0·1596	5·8170	0·5572	,,	
Naja bungarus	0·0512	0·1350	0·0403	S. Ghosh	0·0033
,,	0·0536	0·1430	0·4070	,,	,,
Naja tripudian	0·0553	1·6510	0·4564	H. Bhattacharya	0.03
,,	0·0713	2·1390	0·4585	,,	,,
Bungarus fasciatus (i)	0·1472	0·2770	0·0288	T. C. Sarkar	
,, (ii)	0·1057	0·1640	0·0237	,,	
,,	0·1528	0·2380	0·0238	P. Rây	0·37
,,	0·1664	0·2690	0·0247	,,	

P. RÂY

TABLE II (contd.).

Venoms.	Wt. of venom.	ZnQ$_2$.	Zn.	Analysed by.	Toxicity value.
Bungarus ceruleus	0·0579 g.	Trace	« 0·02%	S. Ghosh	0·0009 mg.
Vipera russellii (i)	0·1028	0·2450 mg.	0·0380	S. Ghosh	
,,	0·0860	0·2270	0·0408	,,	0·01
,, (ii)	0·0752	0·2030	0·0410	,,	
Echis carinata	0·0892	1·083	0·1856	S. Ghosh	0·0093
Haemolysin (*Naja naja*) mixed with mineral salts, NaCl etc.	1·0 50% pure haemolysin fraction	Trace	...	S. Ghosh	9 times more active than crude venom for same N-content.
Neurotoxin (i) (*Naja naja*) mixed with mineral salts	0·0515 82% neurotoxin fraction	0·4070	0·11 ≡ 0·15 in neurotoxin	H. Bhattacharya	15 times more active than crude venom for same N-content.
,, (ii)	0·0606 82% neurotoxin	0·1680	0·041 ≡ 0·052 in neurotoxin	,,	17 times more active than crude venom for same N-content.

* ZnQ$_2$=Zinc quinaldinate.

Toxicity values represent the minimum lethal dose for a pigeon 300 g. by weight by intravenous injection.

The results giving values down to 0·025%, demonstrate the sensitivity and the reliability of the method.

My best thanks are due to Dr. B. N. Ghosh of the Department of Applied Chemistry for the supply of neurotoxin and haemolysin fractions of *Naja naja* cobra venom and for determining the toxicity values of the venoms. I express here my thanks also to Mr. A. C. Ray, M.Sc. in the Department of Pharmacology, School of Tropical Medicine, Calcutta, for his kindly supplying me a sample of *Echis carinata* venom. All other venoms were purchased from Drug House Ltd., Calcutta.

ADSORPTION OF MONO- AND POLYBASIC ACIDS BY SUGAR CHARCOAL.

By Kesho Dass Jain and J. B. Jha.

The adsorption of mono-, di- and tri-carboxy acids and bi-salts of dibasic acids by sugar charcoal activated at 800-850° has been studied. Adsorption of solutes, particularly monocaboxy acids, from solution by sugar charcoal follows the ordinary laws of adsorption and is mainly a surface phenomenon as log x and log C curves are straight lines

While studying adsorption of polybasic acids and their acid salts curious adsorption curves of somewhat periodic nature were obtained. Although a considerable amount of work seems to have been done in this direction this fact escaped notice by the previous workers. Sabalitschka and Finger (Dissrtn. Berlin, 1927-28); T. Sabalitschka (*Pharm. Ztg.*, 1924, **72**, 382), Nekrassov (*Z. physikal. Chem.*, 1928, **136**, 18, 379); Dubinin (*ibid.*, 1929, **140**, 81; 1930, **A150**, 145; *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1829), Bruns (*Kolloid Z.*, 1931, **54**, 33), Roychaudhury (*J. Indian Chem. Soc.*, 1931, **8**, 433), and others studied the adsorption of mono- and dibasic acids by sugar charcoal, and all the workers mentioned above obtained smooth curves, showing regularity in adsorption.

While monobasic acids, both aliphatic and aromatic, behaved normally, the adsorption curves obtained from organic and inorganic di- and tribasic acids were invariably somewhat of a periodic nature.

Adsorption curves obtained for the acid salts of dibasic acids also give curves which are similar to those obtained from acids themselves.

Experimental.

Preparation of Sugar Charcoal.—Crystals of cane sugar were carbonised with strong sulphuric acid and repeatedly washed with boiling distilled water till free from acid. It was then dried, ground to fine powder and passed through 120 mesh sieve. It was finally heated in a muffle furnace at 800-850° for nearly an hour. After heating the charcoal was left in a well stoppered bottle out of contact with air. The sample of the charcoal thus prepared left 0·42% of residue on ignition.

Method of Analysis—The adsorption experiments were carried out by weighing exactly 1 g. of the charcoal in clean, dry, glass bottles, similar in size to which 100 c.c. of the acid solution in freshly prepared distilled water were pipetted. The bottles were shaken for the same length of time and kept for about 18 hours, after which the amount of the solute was deter-

mined in the supernatant liquid by usual analytical methods. The original concentration (C_0) was the amount of the solute originally taken in bottles, that in equilibrium with the charcoal is represented by C_e. The amount of adsorption (x) was determined by differences. The experiments were repeated with every care.

Results for adsorption of various acids are recorded in Tables I and II, while that of bi-salts in Table III.
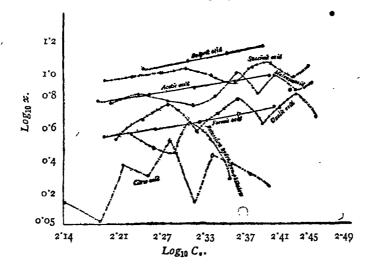
TABLE I.

Dibasic acids.

Adsorption by 1 g. of the charcoal from 100 c.c. of the aqueous solution of acids.

Acids.	C_0.	C_e.	x.	Log C_e.	Log x.
Oxalic	2·9782	1·9255	0·0527	0.4661	$\bar{2}$·7217
	2·8293	2·7554	0·0739	0·4401	$\bar{2}$·8685
	2·6804	2·6193	0·0611	0·4181	$\bar{2}$·7857
	2·5315	2·4832	0·0483	0·3950	$\bar{2}$·6835
	2·3825	2·3132	0·0693	0·3642	$\bar{2}$·8409
	2·2336	2·1771	0·0565	0·3379	$\bar{2}$·7523
	2·0847	2·0410	0·0437	0·3098	$\bar{2}$·6409
	1·9358	1·8710	0·0648	0·2720	$\bar{2}$·8119
	1·7869	1·7348	0·0521	0·2390	$\bar{2}$·7171
	1·6380	1·5988	0·0392	0·2032	$\bar{2}$·5937
Malonic	2·9782	2·8920	0·0862	0·4612	$\bar{2}$·9354
	2·8293	2·7516	0·0777	0·4395	$\bar{2}$·8902
	2·6804	2·5831	0·0973	0.4121	$\bar{2}$·9880
	2·5315	2·4573	0·0742	0·9904	$\bar{2}$·8702
	2·3825	2·3023	0·0802	0·3621	$\bar{2}$·9044
	2·2336	2·1620	0·0716	0·3349	$\bar{2}$·8551
	2·0847	2·0216	0·0631	0·3056	$\bar{2}$·8003
	1·9358	1·8671	0·0687	0·2711	$\bar{2}$·8373
	2·7869	1·7127	0·0742	0·2335	$\bar{2}$·8706
	1·6380	1·5727	0·0653	0·1965	2·8198

TABLE I (contd.).

Acids.	C_0.	C_e.	x.	Log C_e.	Log x.
Succinic	2·9782	2·8671	0·1111	0·4575	$\bar{1}$·0457
	2·8293	2·7346	0·0947	0·4368	$\bar{2}$·9762
	2·6804	2·5645	0·1159	0·4089	$\bar{1}$·0638
	2·5315	1·4211	0·1104	0·3840	$\bar{1}$·0427
	2·3825	2·2937	0·0888	0.3604	$\bar{2}$·9486
	2·2336	2·1344	0·0992	0·3292	2·9967
	2·0847	1·9751	0·1096	0·2956	$\bar{1}$·0402
	1·9358	1·8318	0·1040	0·2630	$\bar{1}$·0172
	1·7869	1·6884	9·0985	0·2275	$\bar{2}$·9936
	1·6380	1·5451	0·0929	0·1889	$\bar{2}$·9682
Phthalic	1·3990	0·3798	0·0192	1·5789	$\bar{2}$·2821
	0·3790	0·3608	0·0182	$\bar{1}$·5573	$\bar{2}$·2608
	0·3590	0·3411	0·0180	1·5329	$\bar{2}$·2542
	0·3391	0·3178	0·0213	1·5022	$\bar{2}$·3249
	0·3192	0·3001	0·0191	$\bar{1}$·4772	$\bar{2}$·2806
	0·2992	0·2767	0.0225	1·4419	$\bar{2}$·3536
	0·2793	0·2661	0·0132	1·4251	$\bar{2}$·1199
	0·2593	0·2426	0·0167	1·3889	$\bar{2}$·2235
	0·2394	0·2204	0·0190	1·3432	$\bar{2}$·2786

FIG. 1.

The results for the adsorption of di- and tri-carboxy acids are given in Tables I and II. It will be seen that the order of adsorption : succinic > malonic > oxalic shows that the adsorption increases with increase in molecular weight, *i.e.*, in favour of the Traube's rule for homologous series.

TABLE II.

Tribasic acids.

Adsorption by 1 g. of charcoal from 100 c.c. of aqueous solution of acids.

Acids.	$C_0.$	$C_e.$	$x.$	Log $C_e.$	Log $x.$
Citric	2·5540	2·5348	0·0190	0·4037	$\bar{2}$·2788
	2·4261	2·4034	0·0227	0·3807	$\bar{2}$·3562
	2·2984	2·2720	0·0264	0·3564	$\bar{2}$·4219
	2·1707	2·1405	0·0302	0·3305	$\bar{2}$·4804
	2·0430	2·0279	0·0151	0.3071	2.1801
	1·9153	1·8776	0·0378	0·2735	2·5769
	1·7877	1·7650	0·0227	0·2468	$\bar{2}$·3553
	1·6599	1·6335	0·0265	0·2131	$\bar{2}$·4229
	1·5323	1.5209	0·0114	0·1821	$\bar{2}$·0562
	1·4646	1·3895	0·0152	0·1429	$\bar{2}$·1816
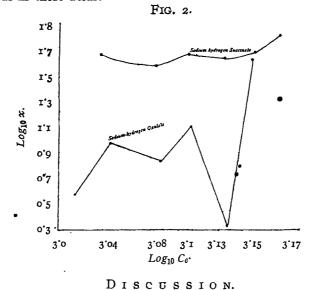
TABLE III.

Bi-salts of dibasic acids.

Adsorption by 1 g. charcoal from 100 c.c. of aqueous solutions of salt.

Bi-salt.	$C_0.$	$C_e.$	$x.$	Log $C_e.$	Log $x.$
Pot. hydrogen phthalate	2·2792	2·2579	0·0213	0·3537	$\bar{2}$·3284
	2·1652	2·1301	0·0351	0·3284	$\bar{2}$·5858
	2·0513	2·0021	0·0489	0·3014	$\bar{2}$·6900
	1·9373	1·9064	0·0309	0·2801	$\bar{2}$·4903
	1·8233	1·7893	0·0341	0·2527	$\bar{2}$·5323

TABLE III (contd).

Bi-salt.	C_0.	$C_{e'}$	x.	Log $C_{e'}$	Log x.
Sod. hydrogen succinate	1·4843	1·4306	0·0537	0·1554	$\bar{2}$·7300
	1·4101	1·3702	0·0399	0·1367	$\bar{2}$·6013
	1·3359	1·2991	0·0368	0·1138	$\bar{2}$·5658
	1·2617	1·2224	0·0393	0·0871	$\bar{2}$·5942
	1·1875	1·1552	0·0323	0·0626	$\bar{2}$·5088
	1·1133	1·0746	0·0387	0·0311	$\bar{2}$·5873
Sod. hydrogen oxalate	1·3775	1·3632	0·0143	0·1345	$\bar{2}$·1545
	1·3086	1·3065	0·0021	0·1159	$\bar{3}$·3304
	1·2397	1·2284	0·0114	0·0892	$\bar{2}$·0558
	1·1709	1·1645	0·0064	0·0660	$\bar{3}$·8062
	1·1020	1·0934	0·0086	0·0387	$\bar{3}$·9340
	1·0331	1·0295	0·0036	0·0124	$\bar{3}$·5587

The results for the adsorption of bi-salts of dicarboxy acids : phthalic, succinic and oxalic acids are given in Table III. From Figs. 1 and 2 the order of adsorption : sodium hydrogen succinate>sodium hydrogen oxalate shows that the adsorption increases with the increase in molecular weight, as in these acids.

FIG. 2.

DISCUSSION.

In the accompanying experiments, we have got irregular curves with polybasic acids, e.g., oxalic, malonic. succinic, phthalic, citric, and with

6

bi-salts of dibasic acids, *e.g.* sodium hydrogen oxalate, sodium hydrogen succinate, and potassium hydrogen phthalate. We had taken all the precautions to avoid contact with oxygen as far as possible. Even if it be granted that a slight oxidation was going on along with the adsorption there is no reason why the curve should be a zigzag one as has been observed. Moreover, chromic and phosphoric acids do not oxidise in which case also irregular curves have been obtained.

Adsorption of monocarboxy acids seems greater than that of dicarboxy acids both in aliphatic and aromatic series. In a homologous series it increases strongly and regularly as we ascend the series. The percentage of adsorption increases as the concentration decreases in monocarboxy acids.

The adsorption curves in case of dibasic, tribasic acids and those of bi-salts of dibasic acids are zigzag,

At present it is not possible for us to fix the cause of irregularities that have been observed. Further work is being done and it is hoped that some explanation might be forthcoming.

The authors are thankful to Professor H. Krall and Professor B. L. Vaish for their encouragement and interest in this work.

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THE DECAY OF HYDROGEN OVERPOTENTIAL AT MERCURY SURFACE.

By S. C. GANGULI.

The decay of hydrogen overpotential was noted against coloured electrode during the electrolylic reduction of maleic and fumaric acids in an aerobic condition A tentative scheme as to the various stages that might occur during the discharge of H ion has been suggested and discussed.

It is well known that a certain amount of overvoltage is necessary to liberate hydrogen at a cathode. Different opinions are held regarding the nature and mechanism of overvoltage as is evident from the good review made by Writz (*Z. Elektrochem.*, 1938, **44**, 303). A knowledge of the rate of decay of overvoltage after switching off the polarising current is obviously necessary to gain a proper insight into the nature of the phenomenon. Little work, however, seems to have been done in this direction, the only important data available being those of Bowden and Rideal (*Proc. Roy. Soc.*, 1928, **A, 120**, 59), who give the rate to be

$$dE_s/dt = k_1 e^{-k_2 E_s}$$

where E_s is the overvoltage, and of Baars (*Ber. Ges. Ford. Naturwiss. Marburg*, 1928, **63**, 213), according to whom the rate of decay is

$$dE_s/dt = -b/t,$$

where "b" is Tafel's constant.

Ghosh and co-workers (*J. Indian Chem. Soc.*, 1933, 9, 43 ; *Biochem. Z.*, 1935, **279**, 296) and Ganguli (*J. Indian Chem. Soc.*, 1937, **14**, 656) recorded the decay of hydrogen overpotential after reducing the oxidant electrolytically at a mercury cathode. In their several experiments the E.M.F. of the cell, Hg-H$_2$/Redox System/o·1N-calomel electrode was actually observed to increase after switching off the reducing current {*cf. J. Indian Chem. Soc.*, 1933, 9, 43, Fig. 2, p_H 7·50(2)}.

During the electrolytic reduction of maleic and fumaric acids at Hg electrode in an aerobic condition with the decay of hydrogen overpotential noted against N/10-calomel electrode, no definite potential corresponding to a redox system could be obtained, but the E M.F. of the cell was found to gradually decay to indefinite values corresponding more or less to the
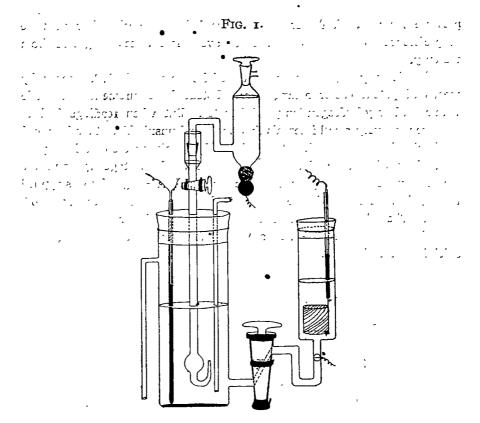
p_H value of the solution. In several cases the E.M.F. was found actually to increase to a maximum after switching off the current and then decay to indefinite values. In absence of any reducible substance, however, the E.M.F. without showing any increase always decays down to indefinite values from the moment the current is switched off.

Experimental.

The main experimental procedure was similar to that described by Ghosh, Raichaudhuri, and Ganguli (loc. cit.). The solution after proper de-aeration was cathodically polarised for requisite duration at a Hg cathode, the polarising current was then cut off and the variation of potential with time was noted.

Scrupulous care was taken to avoid the presence of the slightest trace of extraneous organic matter and oxygen. The ordinary laboratory distilled water was redistilled three times (i) from acid permanganate, (ii) from alkaline permanganate, (iii) from a Jena glass still before use. Sodium sulphate used was strongly ignited in a platinum crucible. Maleic acid and fumaric acid were recrystallised several times from triple distilled water. The greatest difficulty was experienced in obtaining a supply of nitrogen free from organic matters and oxygen as well. Chemically pure nitrogen, prepared from a mixture of ammonium sulphate, sodium nitrite and potassium chromate, was purified by passing through a heated tube containing CuO. It was then passed through a lime tower in which freshly ignited lime was used. The gas was next passed through a heated tube containing palladinised copper in order to free it from the last traces of oxygen, the original Cu/ammonia method having been found unsuitable. The gas was then passed through a saturator and finally into the solution, All glass to glass joints were ground but not greased. They were protected by mercury seals. It is true that lubricators like " Apiezohn " or " Airtite " which are used for high vacuum work have very low vapour pressure, but even they could not be used. Probably, either the solution was spoilt by mechanical contamination or the small amounts of grease that were carried by the nitrogen, which had to be passed for a long time for deaeration, was sufficient to spoil the experiment.

The electrolysing vessel had also to be modified. A Göckel type mercury sealed stop-cock with wide bore (4-5 mm.) was used to join the anode and cathode chambers (Fig. 1). A small platinum wire B was sealed into the anode chamber to serve as an auxiliary cathode. During electrolysis it was connected through a very high resistance to the negative pole
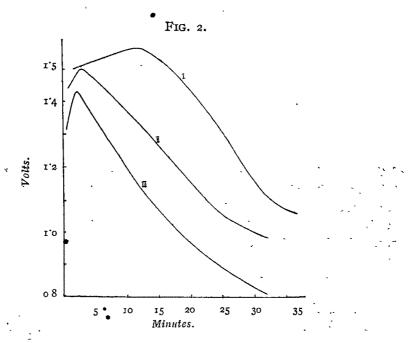
FIG. I.

of the supplying source so that a small negative potential was maintained at this electrode and the diffusion of oxygen from the anode chamber to the cathode chamber was effectively prevented. Both the anode and cathode chambers were tall, so that contact with the rubber stopper could be prevented. It was also essential to start with a dry vessel before beginning the experiment.

The cathode chamber had the usual arrangement. The reference electrode was $N/10$-calomel electrode connected with the solution by a saturated KCl bridge with a mercury-sealed stop-cock and a mercury-sealed ground glass joint. As this does not totally prevent diffusion of oxygen a small current of N_2 was maintained throughout. Every day the apparatus was kept filled up with alkaline permanganate solution after use and before use it was washed with a solution of pure hydrogen peroxide (prepared in the laboratory from pure Na_2O_2 and H_2SO_4, G.R.), hot caustic soda solution and nitric acid and was finally dried in steam.

"Cenco" pure rubber stoppers were used in both the chambers after prolonged boiling in water. Merck's G. R. mercury distilled at a low

pressure was used. A Töpler pump was used for generating low pressure in preference to oil pump in order to avoid last traces of grease from mercury.

The electrolysing current was obtained from a 110 volt D.C. supply by means of potentiometer arrangement. Potential measurements were made with an ordinary hydrogen ion potentiometer. But when readings had to be taken at very small intervals this was found unsuitable. So a balanced triode circuit was designed. Two Phillip's HL_2 valves were used in opposition. It was found that if after keeping the anode voltage 150 and the filament current 0·2 amps a negative potential of $-2·5$ volts was applied to the grids, the current in the grid circuit became negligible (less than 10^{-9} amps). The galvanometer deflections were calibrated by impressing known potentials from a potentiometer at 'X. The usual precautions regarding shielding were observed.

FIG. 2.

A solution containing 10^{-5} M-fumaric acid in $N/10$-sodium sulphate was reduced cathodically for different lengths of time. Fig. 2 gives the variation of E.M.F. with time. Curve I was obtained after electrolysis for 90 seconds, curves II and III for 30 and 20 seconds respectively. Results of similar observations with a solution containing $10M$-fumaric acid in $N/10$-sodium sulphate are shown in Fig. 3. Curve I was obtained after electrolysis for 510 seconds, curve II for 150 seconds and curve III for 54 seconds. In all

cases a current density of 3.33×10^{-4} amps/sq. cm. was used. Below are given two typical data with different concentrations of fumaric acid in $N/10$-sodium sulphate electrolysed for different lengths of time.
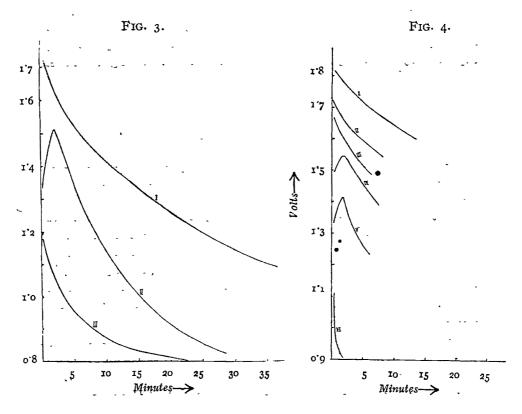
TABLE I.

$10^{-3}M$-Fumaric acid electrolysed for 20 sec.				$10^{-2}M$-Fumaric acid electrolysed for 140 sec.			
Time.*	E.M.F.	Time	E.M.F.	Time *	E.M.F.	Time.	E.M.F.
0 sec.	......	240 sec.	−1.369 volt.	0 sec.	−1.325 volt.	180 sec.	−1.451 volt.
30	−1.320 volt.	420	−1.300	30	−1.372	360	−1.279
60	−1.370	480	−1.241	60	−1.442	840	−1.012
90	−1.402	1050	−0.956	90	−1.472	1740	−0.831
120	−1.425	1800	−0.821	120	−1.498	21300	−0.7725
150	−1.420			150	−1.470		

* (After the current was switched off).   * (After switching off the current).

FIG. 3.

FIG. 4.

Table I shows that when the time for electrolysis is too small (below 54 seconds for 10^{-2}-M fumaric acid) the E.M.F. of the cell decays exponentially after the current is switched off. Only when the time for electrolysis is between definite limits, the E.M.F. of the cell at first rises after switching off the current and then falls.

Effect of Concentration of Reducible Substances.

Fumaric acid of different concentrations was electrolysed for 60 seconds with a current density of 3.33×10^{-4} amp./sq. cm and the rate of variation of E.M F was noted after the reducing current was stopped and the results of such experiments graphically represented in Fig 4

Curves I-VI represent respectively $10^{-5}M$, $10^{-4}M$, $M/500$, $M/250$ and $M/100$-fumaric acid solutions in $N/10$-Na_2SO_4.

From the above figures it will be observed that whenever the E.M.F. of the cell immediately after switching off the current is greater than about 1.50 volts or less than about 1.35 volts, the E.M.F. of the cell decays exponentially with time after the current is switched off. But if the E.M.F. is between these two limits, it at first rises after switching off the current and then decays.

If any reducing substance be not present, the E.M.F. of the cell rises rapidly during electrolysis and when the current is stopped it decays exponentially without passing through a maximum. Owing to the experimental difficulties involved, the effect of change of p_H value of the solution was not very clear. The effect was however very small, if any at all.

DISCUSSION.

During electrolysis the processes that may take place at the cathode are (i) discharge of hydrogen ions, (ii) reduction of the reducible substances present, and (iii) discharge of sodium ions.

Heyrasymenko (*Rec. trav. chim.*, 1935, **44**, 303) found that the deposition of Na on a Hg electrode does not start until the cathode is about 2 volts negative to the $N/10$-calomel electrode. Since the rise and fall of E.M.F. is observed when the E.M.F. of the cell is 1.30 to 1.50 volts, it is obvious that under experimental conditions no Na^+ was discharged on the mercury electrode. Only the processes nos. (i) and (ii) as mentioned above occurred in this case.

The following stages may be supposed to occur during the discharge of hydrogen ions : (i) movement of the ions upto the electrode, (ii) neutralisation by the transfer of an electron from the cathode to the ion, (iii) dehydration, (iv) adsorption of the hydrogen atom produced on the cathode

surface, (v) combination of the atoms produced to form H_2 molecules, and (vi) evaporation of the hydrogen molecules so formed.

The above represents only a tentative scheme. All of them may not take place in the order given and some of them may be simultaneous. According to Tafel (Z. physikal. Chem., 1905, 50, 641) hydrogen over-voltage is due to the slow speed of the reaction taking place in stage (v). On the other hand Volmer, Erdey Gruz and their collaborators (Z. physikal. Chem., 1930, A, 150, 203; 1932, 162, 53) and many others think that the bottle neck is at stage (ii), and is the cause of hydrogen overvoltage. In our discussions we shall assume that neither of the stages are instantaneous and both have comparable velocities.

Since the hydrogen ions move faster than sodium ions, most of the positive current in the solution is carried by the hydrogen ions to the cathode. The main bulk of the solution thus becomes comparatively poor in hydrogen ions whereas the region near the cathode-electrolyte interface receives a large amount of these ions. Owing to the slow speed of transference of electrons from the electrodes to the ions, all of them are not immediately neutralised. There is thus an excess of hydrogen ions near the cathode-electrolyte interface. When the polarising current is stopped, this excess of hydrogen ions diffuses towards the bulk of the solution, thus causing a rise in the E.M.F. after switching off the current. On the other hand, the hydrogen atoms that accumulated on the electrode during electrolysis will combine to form H_2 molecules and evaporate as such for some time after the current is switched off. The E.M.F. of the cell will tend to fall owing to this. Owing to these two opposing tendencies the E.M.F. may at first rise and then fall.

The rate of diffusion of hydrogen ions from the immediate neighbour-hood of the cathode-electrolyte interface to the bulk of the solution will depend on the concentration gradient of the hydrogen ions. According to Bowden (Trans. Faraday Soc., 1928, 24, 473) when the E.M.F. is above 1·60 volts, the interface is comparatively depleted of hydrogen ions by discharge. Hence above 1·60 volts diffusion of hydrogen ions towards the interior will be slow and the rate of increase in E.M.F. due to diffusion will also be small. Again if the surface concentration of H atoms on the cathode reaches very high values, the reaction $2H = H_2$ becomes rapid and the rate of fall in E.M.F. owing to this reaction may under this condition exceed the rate of rise in E.M.F., so that the E.M.F. of the cell will begin to decay exponentially immediately after the current is switched off.

We can now distinguish two sets of circumstances :

(i) *When no reducible substances are present.* Under these circum-stances all the hydrogen atoms that are discharged accumulate on the electrode and the concentration of H atoms rapidly reaches high values. This is what happens when no reducible substances are present and a solution of pure sodium sulphate is electrolysed. The E.M.F. of the cell becomes high very rapidly (more than 1·60 volts) and then decays exponentially after the current is switched off. If some reducible substances are present, a part of the hydrogen is consumed by them and a low hydrogen atom concentration on the electrode is maintained for a longer period.

(ii) *If prolonged electrolysis is carried out.* Under this circumstances (when the voltage is above 1·60) the interface region becomes comparatively depleted of hydrogen ions whereas a large amount of hydrogen ions accumulate on the electrode. Rate of fall of E.M.F. now exceeds the rate of rise. So we obtain an exponential fall in the E.M.F. from the very beginning. Again when the time for electrolysis is very small, the hydrogen ions in the immediate neighbourhood of the electrode are discharged, but a sufficient number do not arrive from the interior to establish an appreci-able concentration gradient. Hence in this case also we shall not obtain any rise of E.M.F.

It is to be noted in this connection that we cannot obtain this pheno-menon when electromotively active normal redox systems such as methylene blue system or ferrous-ferric system are electrolysed since they rapidly establish stable potentials characteristic to themselves. It is only when some electromotively inactive system such as maleic acid or systems whose electrode reactions are slow such as cystine are reduced cathodically, that we may expect to observe such rise and fall of E.M.F.

Hammet (*Trans. Faraday Soc.*, 1933, 29, 770) was the first to suggest that both the electrode processes, $H(H_2O)_n^+ + e = H + nH_2O$, and $2H = H_2$ are slow and of comparable velocities. Loschkarev and Cossin (*Acta Physicochimica*, 1938, 8, 189) have further extended this idea. The observations made in the foregoing experiments appear to agree with this view so far as mercury surface is concerned.

THE ELECTRODEPOSITION OF NICKEL ON IRON AND THE EFFECT OF COLLOIDS ON THE NATURE OF DEPOSIT.

By V. S. Puri and F. R. Mahmood Alvi.

The action of different inorganic colloids, both of elements and salts, on the electro-deposition of nickel on iron has been found to have a very good effect in so far as they give hard lustrous deposits with minimum number of pits. Prussian blue sol comes next in order. The formation of pits has been discussed.

The action of inorganic colloids on the electrodeposition of nickel on copper has been investigated in this laboratory (Puri and Bhatia, *J. Indian Chem. Soc.*, 1939, **16**, 71). It was seen that the colloids can be classified under two heads, *viz.*, those which have a beneficial effect and those which, give dark, loose and spongy deposits. The present work was undertaken to study the effect of addition of colloids on the electrodeposition of nickel on iron. It is of a very great technical importance as the process has extensive applications in industry. For this purpose the final product should be non-rusting and capable of taking a high degree of polish. Further, the layer of nickel should not corrode easily. Various colloids were tried to achieve these ends and the results of our experiments are given in the present paper.

Experimental.

The bath solutions and apparatus employed were the same as those used by previous workers (*loc. cit.*). The electrodes were subjected to a preliminary cleansing treatment given below :

Iron Plate (Cathode).—The iron strip $(6'' \times 1'' \times 0.2'')$ was taken and rubbed on a No. 7 grinding wheel in order to remove the rust stains and to obtain an even, uniform surface. It was then rubbed with sand paper No.$1\frac{1}{2}$ across the lines, and then with No. o until the plate was smooth to touch. It was finally rubbed on a felt bob.

The plate was then boiled in a concentrated solution of sodium hydroxide to remove grease and pickled in a 10.1% solution of sulphuric acid for one minute and washed with distilled water. It was dried in a cold blast of air.

Nickel Plate.—(*Vide* Puri and Juneja, *J. Indian Chem. Soc.*, 1940, **17**, 581).

The bath was kept in a thermostat regulated at 25° and connected in series with a copper voltameter. A current of 0·30 amp. was passed.

Preparation of Colloids.

Silver Sol.—One type of silver sol was prepared by Bredig's electrical dispersion method and an olive-green solution was obtained. This solution after about a week's standing changed to a clear reddish brown liquid with some sediment at the bottom. The other type of silver sol was the same as that used by Puri and Bhatia *(loc. cit.)*.

Red Gold Sol.—Gold chloride (1 g.) was dissolved in water and the solution neutralised by cautious addition of sodium carbonate and the volume made up to 100 c.c. to give a 1 % solution. This solution (10 c.c.) was taken in a pyrex flask and made up to 100 c.c. 3 C.c. of 0·1% solution of tannin were added to this gradually and a ruby red gold sol was obtained immediately.

Blue Gold Sol.—This solution was obtained by reducing gold chloride with hydrazine hydrate prepared in the laboratory. The sol obtained thus was blue.

Sulphur Sol.—*Vide* Puri and Juneja *(loc. cit.)*.

Prussian Blue Hydrosol—Puri and Bhatia *(loc. cit.)*.

Silver Iodide (Positive) Sol.—To 40 c.c. of 0·05N-silver nitrate solution 11 c.c. of 0.1N-KI solution were added drop by drop while the flask was being shaken thoroughly and continuously. A concentrated sol of AgI; green yellow in colour, was obtained.

Silver Iodide (Negative) Sol.—To 220 c.c. of 0.05N-KI solution, 18 c.c. of 0·1N-AgNO₃ solution were added. The colour of the AgI sol was just the same as that of the AgI positive sol. Silver chloride and silver bromide sols were similarly prepared.

Effect of Colloids.

Silver Sol (Bredig's electrical dispersion method).—The amounts used were 4, 8, 12 and 16 c c. of the solution. The deposit became firm with 4 c.c. and still more so with 16 c.c. of the colloid. However, it was not uniform near the bottom of the plate. The number of pits was reduced.

Silver Sol (Tannin method).—The amounts used was 4, 8, 12 and 16 c.c. 4 C.c. of colloidal solution contained 0·000864 g. of silver. The deposit was bright and lustrous in all cases and it could take on a high polish. With 4 and 8 c.c. the deposit was fairly hard but the addition of 12 and 16 c.c. of the colloid gave a uniformly thick and the hardest deposit. The

number of pits was successively reduced in all the cases. Unlike the sol obtained by Bredig's method, the pits had a conch-like appearance (Fig. A).

Red Gold Sol.—The deposit was bright and lustrous and could be given a high degree of polish. Also, it was hard, coherent and would not peel off easily. With 4 c.c. *i.e.* 0·000696 g. of gold large pits were obtained. They were, however, very few in number. Upto 12 c.c. the number of pits increased, after the addition of 16 c.c. the number of pits did not appreciably alter. In outline the pits resemble the conch (*cf.* Cymboliste, *Trans. Electrochem. Soc.*, 1936, 70, 16), but in structure they take after those obtained with the Prussian blue sol. They have a central high spot alternating with elliptical rings and a light annular ring between the two

Blue Gold Sol.—The addition of this colloid caused an increase in the lustre in the order 16 c c. (*i.e.* 0·00032 g. of gold) > 4 c.c. > 8 c.c. > 12 c.c. With 16 c.c. the deposit became very hard. There were a few 'trailing' globules in the deposit which was otherwise found to be fairly thick and and firm. With 12 and 16 c.c. there were no pits on the obverse side and very few on the reverse side.

Sulphur Sol.—The deposit was formed in patches. It had a burnt appearance and lacked lustre in all the cases. Except for the patches of the deposit the remaining areas were covered with clusters of coarsely crystalline nickel which could be easily detached from the plate. It was observed that the sol had been adsorbed and could not be washed away with carbon disulphide. With 16 c c. (*i.e.* 0·000704 g. of sulphur) of the sol the deposit became loose and spongy and a portion of it fell into the bath. Fig. B shows the nickel crystals on the cathode, with adsorbed sulphur, highly magnified.

Prussian Blue Hydrosol —Lustre increased with increasing amounts of the colloid. The plate could take a good polish It was uniformly hard except with 16 c.c. of the colloid when it became less firm. Small globules of nickel were, however, found scattered all over the surface with 4 c.c. *i.e.* 0·000264 g. of the colloid and 'pitting' occurred near the bottom. With 8 c.c. their number decreased. With increased amounts of the sol a few large pits could be discerned. The 'pits' were circular and very deep. Fig. C shows them to consist of a round dark spot surrounded by a lighter annular ring. The colloid was found embedded in the substance of the electro-plate. The colloid could not be easily washed off.

Silver Iodide Sol (Positive).—With 4 c.c. *i.e.* 0·01504 g. of AgI the plate became lustrous at places. It had a burnt look ; scattered shiny black patches appeared with increased amounts of colloid. The deposit was loose.

and crystals of nickel concentrated on the edges. Large areas were not plated at all.

Silver Iodide (Negative), Silver Chloride and *Silver Bromide* sols behaved in a like manner.

Pits during the Process of Formation.

While examining the effect of blue gold sol an insight was afforded into the mode of formation of pits. Fig. D shows two of these pits which are beginning to be formed. The furrows appear to be quite deep. The open end of the horizontal V is then closed forming a unit pit. The limbs then further sheet out in order to from the 'compound' pit (Fig. E). The wings, next, complete the outline of the 'compound' pit. Further developments now take place in the enclosed area which is gradually excavated until it takes the final shape of the depression or a pit.

It may be mentioned here that the effects produced in every case discussed above are from colloidal suspensions and not from the sols in the general sense of the word. As the bath is highly electrolytic in nature the presence of such a suspension is inevitable but it has been observed that this suspension takes days to settle and if stirring is constantly done it settles hardly at all. That the colloids have a marked effect on the amount and nature of deposit appears to be beyond any doubt.
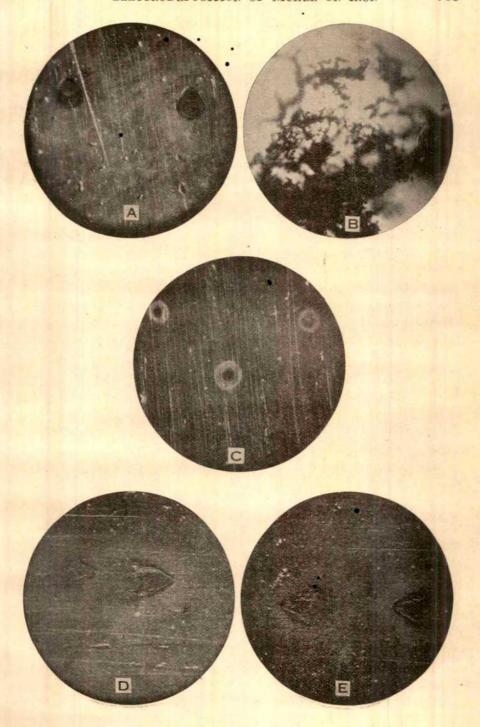
DISCUSSION.

Two types of colloids were tried namely the colloidal elements and salts in the colloidal state. The silver and gold sols were found to have a beneficial effect in so far as they gave hard and lustrous deposits. The number of pits also decreased. The Prussian blue hydrosol comes next in order of efficiency. It gives bright deposits which are capable of taking a high polish.

The halides of silver and elements like sulphur give results which are least satisfactory from the point of view of their utilization in industry.

It has been noticed that with blue gold sol the number of pits decreases with the increase in concentration of the colloid. It is very difficult to to offer an explanation for the formation of pits. The explanation given by some workers that pits are formed under the seat of a bubble of hydrogen gas, which is evolved in the electrolysis, seems to be incorrect for two reasons :

(1) That the gas bubbles were not allowed to settle on the cathode and still the pits appeared.

(2) That where a few bubbles were allowed to remain, they were kept under observation and after the completion of the experiment pits were not necessarily underneath them.

Where a pit is found under the seat of a hydrogen bubble, it is probable that impurities in the cathode plate cause polarization, owing to local differences of potential, with the consequent formation of a pit and the evolution of hydrogen gas.

It appears, however, that the initial condition of a plate, as far as surface texture is concerned, does not affect the formation of a pit. Work is still in progress in this laboratory.

DEPARTMENT OF CHEMISTRY,
    GOVERNMENT COLLEGE,   *Received August* 9, 1940.
        LAHORE.

ROLE OF MANGANESE IN THE BIOLOGICAL SYNTHESIS OF ASCORBIC ACID. THE SYNTHESIS OF INDOPHENOL REDUCING SUBSTANCES BY GUINEA-PIG LIVER *IN VITRO* AND *IN VIVO*.

By M. N. Rudra.

The ability of normal guinea-pig liver to synthesise indophenol-reducing substances *in vitro* and *in vivo* in presence of adequate concentrations of manganese has been demonstrated. A hypothesis that the inability of the guinea-pig and the primates to synthesise ascorbic acid within the body is due to insufficiency of manganese, which acts in the capacity of a co-enzyme in the tissues, has been advanced. The probability of synthesis of ascorbic acid in human being under certain suitable (generally acid) conditions has been discussed.

Guha and Ghosh (*Nature*, 1934, **134**, 739) reported that rat-liver could synthesise ascorbic acid from mannose *in vitro* and *in vivo*. They also reported (*Nature*, 1935, **135**, 234) that normal or scorbutic guinea-pig tissue could not apparently synthesise ascorbic acid from mannose but that embryonic guinea-pig tissue and the ovarian tissue of the pregnant guinea-pig could synthesise ascorbic acid from mannose. They also claimed that only mannose can act as a precursor and although glucose gave some positive results *in vivo* experiments, they opined that the sugar must pass through a mannose-like configuration before it is synthesised into ascorbic acid. The claim of Guha and Ghosh (*loc. cit.*) regarding the synthesis of ascorbic acid from mannose by rat-liver has been challenged by others (Euler, Gartz and Malmberg, *Biochem. Z.*, 1935, **282**, 399 ; Hawthorne and Harrison, *Biochem. J.*, 1937, **31**, 1061 ; Klodt, *Arch. Exp. Path. Pharmacol.*, 1938, **189**, 157 ; Mentzer and Urbain, *Compt. rend. Soc. Biol.*, 1938, **128**, 270). Sztareczy (*Biochem. Z.*, 1938, **295**, 369) concludes that *l*-sorbose and to a less extent mannose can act as ascorbic acid precursors in the rat-intestine (*cf.* also Lemos, *Compt. rend.*, 1939, **208**, 946).

The author (*Nature*, 1939, **143**, 881) has shown that manganese is a determining factor in the synthesis of ascorbic acid by rat-liver and has suggested an explanation of the inability of other investigators (Euler *et al*, *loc. cit.*) to demonstrate the synthesis of ascorbic acid *in vitro* or *in vivo* by rat-liver. It has also been shown by the author that not only mannose but other sugars like galactose and glucose can also act as precursors. It has now been found that normal guinea-pig liver also can synthesise ascorbic acid from the sugar precursors *in vitro* and *in vivo* in presence of adequate concentrations of manganese.

8

Experimental.

Experiments in vitro.

To demonstrate the synthesis of ascorbic acid by normal guinea-pig liver *in vitro*, the experiments of Hawthorne and Harrison (*loc. cit.*) were repeated with guinea-pig liver and with the modification that the Ringer-Locke solution in which the minced liver was incubated for demonstrating the synthesis of ascorbic acid, contained various concentrations of manganese as manganese chloride. Mannose and galactose were employed as precursors. The results are given in Table I.

TABLE I.

In vitro.

Mn in Ringer-Locke.	incubated-mixture.	Sugar.	Ascorbic acid content of liver after 3 hours' incubation (mg./g).	Remarks.
1. 0·10%	0·05%	Mannose	0·18	—
0·02	0·01	,,	0·16	—
0·01	0·005	,,	0·15	—
0·002	0·001	,,	0·14	—
Nil	Nil	Nil	0·14	Control; with liver but no sugar.
2. 0·10	0·05	Mannose	0·18	—
0·02	0·01	,,	0·16	—
0·01	0·005	,,	0·15	—
0·001	0·0005	,,	0·14	—
Nil	Nil	Nil	0·14	Control.
3. 0·10	0·05	Mannose	0·20	—
0·02	0·01	,,	0·16	—
0·01	0·005	,,	0·14	—
Nil	Nil	Nil	0·14	Control.
Fresh liver without incubation.			0·22	—
4. 0·10	0·05	Galactose	0·17	—
0·02	0·01	,,	0·15	—
0·01	0·005	,,	0·13	—
Nil	Nil	Nil	0·13	Control.
Fresh liver without incubation			0·22	—

The results obtained with the incubated tissues are comparable among themselves. Values obtained with the fresh tissue without incubation are naturally higher as incubation causes some loss of ascorbic acid due to oxidation.

Experiments in vivo.

Animals of the same litter and of the same sex were employed for these experiments. Depending upon the weight of the animals, 25 mg. or 40 mg. of mannose contained in 0·5 c.c. or 1 c.c. respectivety of dilute manganese chloride solution were injected intraperitoneally. In the controls,same volume of normal saline was similarly given. The animals were killed 8 hours or 5 hours after injection and the ascorbic acid content of the liver determined by the microchemical method with 2 : 6-dichloro-phenol-indophenol. The titrations (as well as the *in vitro* titrations) were done under ice and were finished in equal time by timing with a stopwatch. In one case a very dilute solution of manganese only was injected. The results are given in Table II.

TABLE II.

In vivo.

Exp. (Intraperitoneally).	Mg. of ascorbic acid per g. of liver.	Remarks.
1. 25 Mg. of mannose in 0·5 c.c. of 0·05% Mn (as MnCl2).	0·30	Killed after 8 hrs.
0·5 c.c. normal saline (N.S.)	0·24	—
2. 25 Mg. of mannose in 0·5. c.c. of 0·04% Mn.	0·27	Killed after 5 hrs.
0·5 c.c. N.S.	0·21	—
3. 40 Mg. of galactose in 1 c.c. of 0·04% Mn.	0·25	,,
40 Mg. of mannose in 1 c.c. of 0·02% Mn.	0·24	,,
1 c.c. N.S.	0·21 .	—
4. 40 Mg. of mannose in 1 c.c. of 0·02% Mn.	0·24	,,
1 c.c. N.S.	0·21	—
5. 0·5 C.c. of 0·001% Mn.	0·22	—
0.5 c.c. N.S.	0·22	—

DISCUSSION.

In this work we have proceeded with the assumption that under the conditions of our experiments, the indophenol titration would give the value for true ascorbic acid. The author does not, thereby, exclude the possible synthesis of non-specific indophenol-reducing substances. The investigation on this problem is proceeding and the synthesis of non-specific reducing substances, if any, will be the subject matter of a subsequent work to be taken in hand.

It will be seen that normal guinea-pig liver can synthesise appreciable

amounts of ascorbic acid (up to 0˙06 mg. per˙g. of liver) *in vitro* as well as *in vivo*. Mannose and galactose can function as precursors. It is conceivable that other sugars may also play the role of precursors (*cf.* also Rudra, *loc. cit.*) In conjunction with the results obtained by the author and reported earlier (*Nature*, 1939, **143**, 881 ; *Biochem. Z.*, 1939, **301**, 268) it is now fairly convincingly proved that manganese is an important link in the mechanism by which the precursors (at least the sugar precursors) are converted into ascorbic acid, manganese acting as the co-enzyme to the dehydrogenase acting on the hexoses. It is interesting to note that Edlbacher and Baur (*Z. physiol. Chem.*, 1938, **254**, 275) found that arginase acts in association with manganese and other metallic ions and they found that manganese is the co-enzyme of arginase and is present with a protein carrier. It would also appear that the enzyme or the enzymes (dehydrogenases) which transform the precursors into ascorbic acid, is present in the guinea pig tissue but its inability to synthesise ascorbic acid *in vivo* is due to lack or insufficiency of manganese in the tissues. This theory is also corroborated by the findings of Lund, Shaw and Drinker (*J. Exp. Med.*, 1921, **33**, 231) who could not detect any manganese in guinea-pig tissues. The author has also found that guinea-pig liver is much poorer in manganese content than the liver of the goat and the fowl. These results will be communicated in due course.

In the light of the author's investigations it would now be possible to explain the inability of the primates and the guinea-pig to synthesise their requirements of ascorbic acid within their bodies like other animal species. This inability can be explained, as already indicated, by the absence in the tissues of sufficient manganese which is the co-ferment of the dehydrogenases responsible for the conversion of the precursors into ascorbic acid. The author also advances the hypothesis that under favourable conditions, man would be able to and does synthesise certain amounts of ascorbic acid within the body.

The precursors and the enzymes are there and only the co-enzyme manganese is not present sufficiently to make the enzyme active. Any condition, therefore, which favours the absorption of greater amounts of manganese by the tissues will also help them to synthesise ascorbic acid *in vivo*. Oleson (*Biochem. Z.*, 1934, **269**, 329) found that in soils and in water cultures plants assimilate greater amounts of manganese when the reaction is acid. It is probable that an acid reaction in the small intestines will similarly lead to a greater absorption of manganese by the animal tissues and they would then be able to synthesise ascorbic acid.

Among the factors influencing the reaction in the intestines are the

nature of the diet and its acid-base balance. Carbohydrate diets make the intestinal reaction strongly acid and meat diet also gives an acid reaction. The grain food of birds and flesh food of animals and carrion eating birds thus contribute to an acid intestine resulting in manganese absorption with consequent synthesis of ascorbic acid. Robinson (*J. Biol. Chem.*, 1935, **108**, 403) has shown that irrespective of the reaction of the solution introduced into the jejunal loop of a dog, the recovered solution had always a pH of about 6·5. Rat intestines were also found to have a reaction of the mean value of about pH 6·5. Redman, Willimot and Wokes (*Biochem. J.*, 1927, **21**, 589) as well as Abrahmson and Miller (*Proc. Soc. Exp. Biol. Med.*, 1925, **22**, 438) could not get any marked variation in the intestinal pH of rat by varying the diet. The rat and the dog have thus a constant and acid intestine which enables them to absorb sufficient manganese resulting in ascorbic acid synthesis by the animals. It is probable that manganese is absorbed in the lower jejunum and upper ileum where the reaction is acid in the rat and the dog and alkaline in the guinea-pig. This explains the ability of the rat and the dog and the inability of the guinea-pig to synthesise ascorbic acid *in vivo*. The same arguments hold in the case of other animal species which synthesise ascorbic acid. In the case of man, the intestinal reaction will be governed by the nature of his diet and its acid-base balance. If and when the reaction in the small gut becomes acid, sufficient manganese will be absorbed resulting in synthesis of certain amounts of ascorbic acid. Harde and Wolff (*Compt. rend. Soc. Biol.*, 1934, **116**, 288) think that the small intestine is the seat of ascorbic acid synthesis (*cf.* Hopkins, *Chem. Ind.*, 1934, **53**, 874). Hopkins and Slater (*Biochem. J.*, 1935, **29**, 2803) think that both the liver and the small intestines are the seats of ascorbic acid synthesis in the rat. The author's view is that in animals in whom ascorbic acid synthesis occurs, most of the synthesis occurs in the region of manganese absorption, that is, in the lower jejunum and upper ileum.

Certain sections of the Indian people with grossly inadequate intake of ascorbic acid (according to generally accepted standards) do not show any signs of scurvy. This can be explained by their "acid" and carbohydrate-rich diet which makes intestinal reaction acid with consequent ascorbic acid synthesis within the body due to sufficient manganese absorption. Wilson and Mitra (*Indian J. Med. Res.*, 1938, **26**, 131) carried out some diet surveys in which the garden labourers with an intake of only 26 mg. of ascorbic acid, contained in raw vegetables consumed after thorough cooking, showed no signs of vitamin C deficiency. The actual amounts of ascorbic acid consumed could not be more than 10 to

13 mg. An interesting result was obtained by Hawley, Frazer, Button and Stevens (*J. Nutrition*, 1936, **12**, 215) by the ingestion of ammonium chloride and sodium bicarbonate respectively to normal healthy persons. They found greater excretion of ascorbic acid in the former case than in the latter. This greater excretion of ascorbic acid in the urine of persons taking ammonium chloride was due, according to the author's theory, to the acidification of the small gut, absorption of more manganese than normally and synthesis of some ascorbic acid by the subjects.

Rietschel (*Klin. Wschr.*, 1938, **17**, 1787) points out that most of the German people do not take more than 10 to 15 mg. of ascorbic acid in the winter and in the spring and yet show no signs of scurvy. He postulates that human requirement is small owing to the alternate oxidation and reduction of ascorbic acid in the body. In a further study by Rietschel and Menschig (*Klin. Wschr.*, 1939, **18**, 273), the latter lived on a diet of meat and cereals, cooked with alkali, for 100 days and remained well and free from scurvy. Although serum ascorbic acid fell gradually, the urinary output was normal, 1·0 mg. per 100 c.c. towards the end of the investigation. They explain the non-appearance of scurvy symptoms by Rietschel's previous hypothesis of alternate oxidation and reduction of ascorbic acid in the body. A more plausible explanation, according to the theory of ascorbic acid synthesis in man just postulated, would be that there is some synthesis of ascorbic acid by the subject during the test period. Although Stepp and Schroeder (*Klin. Wschr.*, 1939, **18**, 484) discount the possible synthesis of ascorbic acid in man because in the test by Rietschel and Menschig, the serum ascorbic acid fell to 0·06 mg. per 100 c.c. at the end, this can be explained by the supposition that the amount synthesised was wholly metabolised and passed into urine and, therefore, could not raise the serum ascorbic acid content. Rudra's hypothesis on the synthesis of ascorbic acid in man is supported by the fact that generally more ascorbic acid is excreted in urine in acid conditions than in alkaline conditions.

The conclusion of Wright (*Lancet*, 1900, *ii*, 565 ; 1908, *ii*, 725) that scurvy goes with acidosis cannot be given serious consideration. Lepper and Zilva (*Biochem. J.*, 1925, **19**, 581) have shown that although plasma bicarbonate in scorbutic guinea-pigs is slightly lower than that in normal animals, owing to the absence of Na and K in scorbutic diets, the pH of the plasma of scorbutic guinea-pigs is practically the same as the pH of the normal ones ; the former being just a shade higher than the latter which fact clashes with Wright's conclusion but does not disprove the author's hypothesis. The fact that manganese content of human tissues is practically constant throughout life does not clash with

the claim of many investigators (Giroud, Ratsimamanga, Robinowicz, Ruiz and Cesa, *Compt. rend. Soc. Biol.*, 1936, **123**, 1038 ; Rohmer, Sanders and Bezssonoff, *Nature*, 1934, **136**, 142 ; Banerji, *Curr. Sci.*, 1935, **3**, 355) that in the early months of infanthood, ascorbic acid synthesis occurs. Sheldon and Ramage (*Biochem. J.*, 1933, **27**, 674) found that considerably more manganese is found in meconium than can be found in the tissues. The excess of manganese is not explained. The gall bladder was richer in manganese than the liver. It is probable, the small intestines of the newborn babe would have been found, if examined, to be richer in manganese than the adult tissue. This would explain the possible synthesis of ascorbic acid in early infanthood and during the later stage of foetal life and inability later when most of the manganese stored in the intestines is exhausted. (*cf.* also Ramage, Sheldon and Sheldon, *Proc., Roy. Soc.*, 1933, **B, 113**, 300).

A preliminary report of this investigation appeared in *Nature*, 1939, **144**, 868).

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RADIOACTIVE ORGANIC BROMO COMPOUNDS.

By S. D. Chatterjee and D. K. Banerjee.

A few radioactive bromo compounds have been prepared and the yield of the radi active materials in the compounds determined.

The use of artificially radioactive substances in botanical and biological investigations is increasing very rapidly. Hevesy and others (*Nature*, 1936, **137**, 66 ; 1935, **136**, 754) used radioactive phosphorus to trace the course of phosphorus in the body of plants and animals. Recently, attention has been drawn to the preparation of radioactive organic bromo compounds by Friedmann, Solomon and Werthessen (*Nature*, 1939, **143**, 472) and they propose to use them in biological experiments. An account of some of our experiments along similar lines is described below.

The radioactive isotope Br^{80} has been chosen by us because it has a conveniently long half-life ($4 \cdot 2$ hours) and is chemically reactive. The large water-sensitivity of the radioactive isotope further facilitates our experiments with a compartively weak Ra-Be source. The relative abundance of Br^{79} in natural bromine is also high, being about $51 \cdot 4$ %.

The first technique is the addition of bromine to a double bond. Bromine was introduced to the unsaturated double bond of oleic acid according to the following representation :

$$C_8H_{17} \cdot CH = CH \cdot C_7H_{14} \cdot CO_2H \quad \text{Oleic acid)}$$
$$\downarrow Br$$
$$C_8H_{17} \cdot CH - CH \cdot C_7H_{14} \cdot CO_2H \quad \text{(Dibromo-oleic acid)}$$
$$\overset{|}{Br} \quad \overset{|}{Br}$$

Ethylene dibromide (10g.) was irradiated with slow neutrons from a 60 mc (Ra—Be) source and after irradiation $2 \cdot 9$ g. of bromine were added. Oleic acid (5 g.) was next added slowly with shaking, and ethylene dibromide was distilled off in vacuum. The residue was taken in a thin-walled glass vessel and measurements were made with a thin walled Geiger-Müller counter. The method yielded a high concentration of radioactive material.

In the next reaction studied, bromine was introduced into the benzene ring. Thus, anisole was treated with bromine when bromoanisole was formed.

Anisole (5 g.) was dissolved in ethylene dibromide (100 g.). Bromine (3g.) was then added under cooling and constant shaking. When the characteristic colour of bromine just disappeared, ice-cold water was poured into the solution. Thus hydrobromic acid remains dissolved in water and the other layer containing ethylene dibromide and bromo-anisole was separated by a separating funnel. Traces of organic compound were removed from the aqueous layer by shaking with benzene. Hydrobromic acid was precipitated by silver nitrate and the activity of silver nitrate was measured.

The combined benzene and ethylene dibromide solution was throughly washed with dilute alkali to remove hydrobromic acid completely and then washed with water. It was then fractionally distilled, the fraction boiling at 223° being collected and used for the measurement of radioactivity.

It was found that almost equal activity appeared in silver bromide precipitate and bromoanisole solution. The concentration of radioactive material was found to be lower than in the first reaction.

In the next reaction studied acetanilide was treated with bromine when bromoacetanilide was formed and hydrobromic acid liberated.

Acetanilide (5g.) was added to 100 c.c. of irradiated ethylene dibromide and 7 g. of bromine were added with cooling. Shining crystals of p-bromo-acetanilide at once separated out. They were filtered and recrystallised from dilute alcohol, m. p. 131°. The yield of radioactive material was of the same order as that obtained in the case of bromoanisole.

Table I.

Relative radioactivity per g. atom of bromine.

Ethylene dibromide	...	...	...	...	1·0
Dibromo-oleic acid	...	...	...	...	32·5
Bromoanisole	...	...	...	...	8·7
Para-Bromo-acetanilide ...	...	...	...	...	6·5

It may be emphasised, however, that although care was taken to keep the geometry constant, the results can only be taken as qualitative.

A new method for introducing radioactive halogen into organic halides is that of Brejneva, Roginsky and Schilinsky (*Acta Physicochemica*, 1936, **5**, 549). They used radioactive aluminium bromide, well known as a halogenation catalyst, and suggested an exchange between the aluminium and alkyl bromides and, therefore, a method of preparing radioactive organic halides according to the reaction

$$Al_2Br_6{}^* + RBr = Al_2Br_6 + RBr^*$$

where the starred element is the radioactive constitutent.

Our preliminary investigation has shown that phosphorus tribromide is rapidly activated by exchange reactions with irradiated ethyl bromide, *i.e.*, when they are mixed together, the radioactive bromine rapidly distributes itself between them in a ratio of bromine content of these compounds. Now, when an alcohol is treated with this activated phosphorus tribromide, the bromine atoms are quickly incorporated in it forming corresponding radioactive alkyl bromide. A typical experimental result is given :

Ethyl bromide (75 g.) was irradiated with slow neutrons. Phosphorus tribromide (2 g) was shaken with irradiated ethyl bromide for about 15 minutes. Ethyl bromide was then distilled off from a water-bath. The activity of phosphorus tribromide was measured. Next, 12 g. of *iso*amyl alcohol were slowly added to phosphorus tribromide in benzene medium and the container was kept immersed in an ice-bath for about $\frac{1}{2}$ hour and the mixture refluxed for about 15 minutes. Ice and water were then added to the solution so that the excess of phosphorus tribromide broke up into phosphoric acid etc. which were washed up with dilute alkaline bicarbonate solution and water. The alkyl bromide was separated and dried by calcium chloride.

Measurements showed that about 65 % of the activity of phosphorus tribromide had been transferred to the alkyl bromide molecule.

EXPERIMENTS TOWARDS THE SYNTHESIS OF ANALGESICS.

By P. V. A. RAMAN.

The syntheses of 1-(2'-furyl)-3: 4-dihydro-6: 7-methylenedioxy*iso*quinoline, 1- 7'-methoxy 2'-coumaromyl)-3: 4-dihydro-6: 7-methylenedioxy*iso*quinoline, and 1-(9'-phenanthryl)-3: 4-dihydro-6: 7 methylenedioxy*iso*quinoline and their *N*-methyltetrahydro derivatives are reported.

Morphine is recognised as one of the best known natural analgesics. "Euphoria" leads to repeated administration of the drug, which in turn causes "addiction". Innumerable attempts have been made to prepare simple, and easily accessible synthetic substances, having the analgesic activity of morphine, but devoid of its undesirable effects (Small, Mosettig, Eddy and others, *U.S. Public Health Reports, suppl.*, 1938, 138). In morphine there are furan, coumarone, dibenzofuran, *iso*quinoline skeletons present. Any one of these may prove to be the basic structure for its analgesic properties.

Considering morphine as an amino-alcohol Mosettig and co-workers (*J. Amer. Chem. Soc.*, 1933, 55, 3448 ; 1935, 57, 2189 ; 1936, 58, 1570, 1311) have synthesised a large number of simpler amino-alcohols derived from phenanthrene, dibenzofuran and carbazole derivatives, which were found by Eddy and co-workers (*J. Phar. Expt. Therap.*, 1933, 48, 175 ; 1935, 55, 419) to possess some interesting physiological properties. Mosettig and co-workers (*J. Org. Chem.*, 1938, 3, 317 ; *J. Amer. Chem. Soc.*, 1938, 60, 2962 ; 1940, 62, 1110) have also synthesised other substances *e.g.* benzo-quinolines, napthaquinolines, dibenzo*iso*quinolines and naphtha*iso*quino-lines. The former two types of compounds were found to be either weak or entirely ineffective as analgesics (Eddy, *J. Phar. Expt. Therap*, 1936, 58, 159). The above authors prepared 1:2:3:4-tetrahydronaphtha-(1:2h)-*iso*-quinoline and 1:2:3:4-tetrahydrodibenzo-(f:h)-*iso*quinoline by cyclising the formaldehyde condensation products of 2-(2-aminoethyl)-phenanthrene and 9-(2-aminoethyl)-phenanthrene respectively by Decker and Becker method, the Bischler-Napieralski reaction not succeeding (1938, *loc. cit.*)

The present investigations were undertaken to synthesise *iso*quinoline derivatives possessing the structural groups such as furan, coumarone, phenanthrene, etc., from the simpler and easily accessible homopiperonyl-aminé as the starting material according to the following scheme :

Homopiperonylamine, prepared according to Buck and Perkin (*J. Chem. Soc.*, 1924, 126, 1693) has been condensed with (i) ethyl α-furoate

R—CO (I)

(II)

R''/ (III)

Reduction of methoiodide

R—CO OMe (IV)

R'/ OMe (V)

R''/ OMe (VI)

Reduction of methoiodide

R—CO (VII)

R' (VIII)

R'' (IX)

Reduction of methoiodide

R·COCH₂·CH₂|X (O)

(X, X = H; XI, X = Ph)

Homopiperonyl -amine

R = CH₂

R' = CH₂

R'' = CH₂

(Schwanert, *Annalen*, 1860, **116**, 267) ; (*ii*) methyl 7-methoxycoumarone-2-carboxylate; (*iii*) 9-phenanthroyl chloride (Mosettig and Kamp, *J. Amer. Chem. Soc.*, 1933, **55**, 3448) ; (*iv*) ethyl β-2-furylpropionate (Windaus and Dalmer, *Ber.*, 1920, **53**, 2304) and (*v*) ethyl β-2-(5-phenyl)-furyl propionate (Robinson and Todd, *J. Chem. Soc.*, 1940, 1743) to give the amides (I), (IV), (VII), (X) and (XI) respectively. Out of these only the amide (IV), (X) and (XI) are well defined crystalline solids.

The cyclisation of the amides (I), (IV) and (VII) to the corresponding 1-(2'-furyl)-3:4-dihydro-6:7-methylenedioxy*iso*quinoline (V), 1-(7'-methoxy-2'-coumaronyl)-3:4-dihydro-6:7-methylenedioxy*iso*quinoline (V), and 1-(9'-phenanthryl)-3:4-dihydro-6:7-methylenedioxy*iso*quinoline (VIII) respectively, is effected easily and in good yield by gently refluxing with phosphorus oxychloride in dry toluene solution. Attempts to effect the cyclisation of the amides (X) and (XI) under a variety of conditions resulted only in tarry non-basic products. The reduction of the methoiodides of the dihydro bases to the corresponding *N*-methyltetrahydro bases is effected readily by heating on the water-bath with zinc and dilute sulphuric acid. These are oils and are characterised as picrates.

EXPERIMENTAL

1-(2'-Furyl)-3:4-dihydro-6.7-methylenedioxyisoquinoline (II).—A mixture of homopiperonylamine (2 g.) and ethyl furoate (1·53 g.) was heated on the water-bath for 24 hours. An ethereal solution of the reaction product was purified by washing with dilute hydrochloric acid followed by water, drying over anhydrous magnesium sulphate and then removing the solvent. The crude amide, thus obtained, was treated with dry toluene (20 c.c.) and phosphorus oxychloride (10 c.c.). The mixture was gently refluxed for 1 hour (guard tube), cooled and poured with stirring on to crushed ice. The resulting solution after freeing from non-basic impurities by repeated extraction with benzene, was thoroughly cooled, basified with concentrated ammonia, and extracted with ether. The ether extract after drying over anhydrous potassium carbonate and evaporation of the solvent, yielded the dihydro base, which crystallised from dilute alcohol in long, colourless rectangular plates, m.p. 95-96°, yield 1·5 g. (Found : C, 69·39 ; H, 4·49 ; N, 5·86. $C_{14}H_{11}O_3N$ requires C, 69·72 ; H, 4·57 ; N, 5·81 per cent).

The *picrate* crystallised from dilute alcohol in long, shining yellow needles, m.p. 206° (decomp.). (Found : N, 11·93. $C_{20}H_{14}O_6N_4$ requires N, 11·91 per cent).

The *methoiodide* crystallised from chloroform-petrol in short, bright yellow needles, m.p. 238° (decomp.). (Found: I, 34·21. $C_{15}H_{14}O_3NI$ requires I, 33·19 per cent).

1-(2'- Furyl) - N- methyl- 1:2:3:4-tetrahydro- 6:7-methylenedioxyisoquinoline (III).—A mixture of the methoiodide of the dihydro base (0·5 g.), dilute sulphuric acid ·(20 c.c.) and zinc dust (5 g.) was heated on a water-bath till the colour of the solution completely disappeared. The reaction mixture was filtered hot, the residue was washed with hot dilute sulphuric acid and the filtrate after freeing from non-basic impurities by extracting with benzene, was throughly cooled, basified with concentrated ammonia and extracted with ether. The ethereal solution after drying and evaporation yielded the tetrahydro base as a viscous oil which was characterised as the *picrate* crystallising from dilute alcohol in short yellow needles, m.p. 99-100° (decomp.). (Found: C, 51·96 ; H 3·74 ; N, 11·57. $C_{21}H_{18}O_{10}N_4$ requires C, 51·86 ; H, 3·7 ; N, 5·3 per cent).

Methyl 7-Methoxycoumarone-2-carboxylate.—7-Methoxycoumarone-2-carboxylic acid (12 g.), prepared according to the method of Reichstein and co-workers (*Helv. Chim. Acta,* 1935, **18**, 819) was esterified by saturating an absolute alcoholic solution with dry hydrochloric acid. The resulting ester was worked up in the usual way and was crystallised from dilute alcohol in long white needles, m p. 79°, yield 7 g. (Found: C, 63·62 ; H, 4·94. $C_{11}H_{10}O_4$ requires C, 64·07 ; H, 4·85 per cent).

7-Methoxy-2-coumaronylhomopiperonylamide (IV).—A mixture of homopiperonylamine (2 g.) and methyl 7-methoxycoumarone-2-carboxylate (2·5 g.) was heated on a water-bath for 24 hours. After isolation in the usual way, the crude amide was crystallised from toluene-petroleum ether in white clustres of needles, m.p. 86°, yield 3 g. (Found: C, 66·99 ; H, 5·09 ; N, 4·19. $C_{19}H_{17}O_5N$ requires C, 67·25 ; H, 5·01 ; N, 4·13 per cent).

1- (7'-Methoxy-2'- coumaronyl)- 3:4- dihydro-6:7-methylenedioxyisoquinoline (V).—A mixture of 7-methoxy-2-coumaronoylhomopiperonylamide (2 g.), dry toluene (20 c.c.) and phosphorus oxychloride (10 c.c.) was gently refluxed for 1 hour with exclusion of moisture. The reaction mixture after decomposition with crushed ice, was freed from non-basic impurities by extraction with benzene, then thoroughly cooled, basified and the liberated dihydro base extracted with ether. From the dried ethereal solution (potassium carbonate) the dihydro base, obtained as residue, was crystallised from dilute alcohol in long colourless rectangular plates, m.p. 140-42°, yield 1·5 g. (Found: C, 71·31 ; H, 4·61 ; N, 4·44. $C_{19}H_{15}O_4N$ requires C, 71·03 ; H, 4·67 ; N, 4·36 per cent).

The *picrate* crystallised from dilute alcohol in short yellow needles, m.p. 220° (decomp.). (Found: N, 10·13. $C_{25}H_{18}O_{11}N_4$ requires N, 10·18 per cent).

The *methoiodide* crystallised from chloroform-benzene-petrol in orange yellow, long, rectangular plates, m.p. 190-91° (decomp.). (Found : I, 27·78. $C_{20}H_{18}O_4NI$ requires I, 27·43 per cent).

1 *(7'-Methoxy-2'-coumaronyl)-N-methyl-1:2:3:4-tetrahydro-6:7-methylene-dioxyisoquinoline* (VI).—The methoiodide of the dihydro base (1 g.) was reduced with dilute sulphuric acid (20 c.c.) and zinc dust (5 g.) as before. The product after isolation, as described before in an analogous case, was an oil which was converted into the picrate   The *picrate* crystallised from dilute alcohol in dull yellow plates, m.p. 185-87° (decomp.). (Found: C, 55·42 ; H, 3·92 ; N, 10·02. $C_{22}H_{26}O_{11}N_4$ requires C, 55·12 ; H, 3·89 ; N, 9·9 per cent).

1-(9'-Phenanthryl)-3:4-dihydro-6:7 methylenedioxyisoquinoline (VIII).— Homopiperonylamine (2 g.) and 9-phenanthroyl chloride (3 g) were condensed in presence of concentrated potassium hydroxide solution. The resulting amide was extracted with ether, repeatedly washed with dilute hydrochloric acid, water, then dried and the solvent removed by distillation. The crude amide, dry toluene (20 c.c.) and phosphorus oxychloride (10 c.c.) were gently refluxed for 1 hour with the exclusion of moisture. The product was isolated as before.   The oily dihydro base gave a picrate.

The *picrate* crystallised from dilute alcohol in shining yellow prisms, m.p. 145-47° (decomp.). (Found : C, 61·39 ; H, 3·46 ; N, 10·3. $C_{30}H_{20}O_9N_4$ requires C, 62·17 ; H, 3·45 ; N, 9·7 per cent).

1-(9'- Phenanthryl)- N-methyl- 1:2:3:4- tetrahydro- 6:7-methylenedioxyiso-quinoline (IX).—The methoiodide of the dihydro base (0·5 g.) was reduced with dilute sulphuric acid (30 c.c.) and zinc dust (5 g.) as described before. The tetrahydro base, liberated with ammonia, was extracted with ether and the ethereal extract dried (anhydrous potassium carbonate) and the solvent removed by distillation.   The oily base was converted into a picrate.

The *picrate* crystallised from dilute alcohol in dull yellow needles, m p. 105-8° (decomp.). (Found : C, 62·67 ; H, 4·07 ; N, 9·52. $C_{31}H_{24}O_9N_4$ requires C, 62·41 ; H, 4·02 ; N, 9·40 per cent).

β-2-Furylpropionylhomopiperonylamide (X).—A mixture of homo-piperonylamine (2 g.), ethyl β-2-furylpropionate (2·06 g.) was heated on a water-bath for 24 hours. The resulting amide was extracted with ether. The ethereal extract, after washing with dilute hydrochloric acid and water, was dried and the solvent removed. The amide crystallised from dilute

alcohol in short shining needles, m.p. 92°, yield 3 g. (Found: C, 67·33; H, 5·91; N, 3 89.· $C_{18}H_{17}O_4N$ requires C, 66·80; H, 5·92; N, 4·88 per cent).

β-2-(5-Phenyl)-furylpropionylhomopiperonylamide (XI).—Homopiperonylamine (2 g.), β 2-(5-phenyl)-furyl propionate (2·5 g.) were condensed by heating on the water-bath for 24 hours. The resulting amide was purified and separated as in the above experiment The amide crystallised from dilute alcohol in short shining plates, m.p. 104·5°, yield 3 g. (Found : C, 73·1; H, 5·92;. N, 4·05. $C_{22}H_{21}O_4N$ requires C, 74·7 ; H, 5·99; N, 3·87 per cent).

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STUDIES ON THE CATAPHORETIC SPEED OF SOL PARTICLES AS DEPENDENT ON THE REDOX POTENTIAL OF THE LIQUID MEDIUM.

By J. C. Ghosh and N. G. Basak.

Mobility of colloidal particles of platinum and gold in very dilute aqueous solutions of a few redox systems have been studied. Results indicate that the change in the cataphoretic speed and hence the electrokinetic potential of the gold and platinum particles are not probably due to any specific ion adsorption but are due to more general factors the predominant one being the electron activity of the medium which is responsible for the oxidation-reduction potential of the system.

There are few problems in electrochemistry which are of greater theoretical significance than the absolute single potential of metals but about which there is greater uncertainty.

The Helmholtz-Lippman theory that the surface tension of mercury would increase as the cathode polarisation is increased, and would reach a maximum when the potential between mercury and solution has a zero-value gave in the hands of skilful investigators the value of $E_h = -0·277$ as the zero-point of absolute potential (Kruger and Krummrich, Z. Elektrochem., 1913, **19**, 667.)

The same value of the zero-point of absolute potential is also obtained by the use of dropping mercury electrode (Palmaer, Z. physikal. Chem., 1898, **25**, 265 ; 1899, **28**, 257 ; Nernst, Z. Elektrochem., 1906, **12**, 192).

The reliability of the single electrode potentials derived according to the above two methods was not questioned so long as these were the only two methods available. Doubts were cast on this value of single potential by the investigation of Billiter who by careful sampling, investigated the the changes in solution taking place in the vicinity of drop electrodes. Assuming that the observed changes were due to changes in the concentration of Hg^{++} ion, he concluded that the zero point of absolute potential occurs between $E_h = +0·4$ and $E_h = +0·5$ (Billiter, Z. physikal. Chem., 1904, **48**, 513). Similar results have been obtained later by Garrison, Bennewitz and other workers.

According to Freundlich, we must distinguish between (i) the true thermodynamic potential E which is the potential of metal surface against the movable liquid and is due to the reversible transformation :

$$Metal \rightleftharpoons (metal\ ion) + (e)$$

where (e) is the electron concentration, and (ii) the electrokinetic potential which is the potential between the thin liquid film directly in contact with the solid metal surface and adhering firmly to it and the readily movable liquid. Variation of electrokinetic motion and even its reversal only indicate the corresponding changes in ξ potential and may not throw much light on the absolute value of E, the thermodynamic potential.

This objection has also been raised against "Schabe method" of Bennewitz and it is maintained that scraping with an agate edge cannot remove the firmly adhering liquid film from the metal surface and only the outer surface of the electrical double layer can be scraped away.

By studying the effect of concentrations c of salts on the variation of ξ and E for the same surface, it has been possible to show in *some cases* the very marked difference in the $ξ - c$ and $E - c$ curves. Taking advantage of the fact that glass acts like a hydrogen electrode over a wide range of p_H , Freundlich *et al* (*Preuss. Akad. Wiss.*, 1920, 20, 397) have made a direct comparison of the effect of salt on E and ξ. It was found that the $ξ - p_H$ and $E - p_H$ curves of a glass surface covered with a thin film of adsorbed serum albumin in acetate buffers of the same ionic strength had *opposite* slopes.

This is an interesting observation, and it was considered desirable to study the ξ potential of noble metals in a liquid environment whose electron activity is known. It is customary now-a-days to describe oxidation-reduction processes in terms of transference of electrons. In a reversible reaction of the type $AH_2 \rightleftharpoons A + 2H^+ + 2e$, the logarithms of the electron activity is given by the equation

$$\log (e) = \tfrac{1}{2} \log \frac{(AH_2)}{(A)} + \log \frac{1}{H^+} + \text{constant},$$

and the oxidation-reduction potential of a solution containing such a system is a measure of the electron activity and is given by the corresponding equation

$$E_{Redox} = E_0 - 0.03 \log\frac{(AH_2)}{(A)} - 0.06 \, p_H \text{ at } 25^0.$$

We have in this investigation, studied the mobility of colloidal particles of platinum and gold in very dilute aqueous solutions of the following redox systems :

Lauth's violet (thionine), o-bromophenol indophenol, o-chloroindo-2 : 6-dichlorophenol, methylene blue, potassium indigo-tetra-sulphonate and o-cresol indophenol. These dyes have been specially prepared for oxidation-reduction work in laboratories of the British Drug Houses and were

certified to be pure analytical reagents. The potential at p_H 7 varied from $+0.23$ volt in the case of bromophenol to -0.046 volt in the case of potassium indigo-tetrasulphonate. The dyes were also selected with a view to obtaining in some cases positive dye ion, and in others, negative dye ion. The velocity of the particles was measured in an electrophoresis cell of cylindrical cross section in conjunction with a Zeiss Ultramicroscope outfit (Mättson, *Koll.-chem. Beih.*, 1922, **14**, 227 ; Svedberg and Anderson, *Kolloid Z.*, 1919, **24**, 156):

A 500 c.p. Ediswan point-o-lite lamp was used in place of an electric arc for intense illumination of the ultamicroscopic field, as unlike the ordinary arc it did not require any attention during the experiment.

The electron activity of the solution has been varied by changing the ratio of oxidant to reductant and also by changing p_H by the addition of a few drops of a dilute solution of ammonia and acetic acid as the case may be. Buffer solutions cannot be used as they coagulate the solution.

E X P E R I M E N T A L.

The details of experimental arrangement and procedure are given below.

The dye solution (0.005%) was freshly prepared every day. The reduction of the dye has to be effected by reagents which will not increase the ionic strength of the solution, nor should they be so surface active that the colloidal particles get coated with a film of these reagents. After many trials, the following two methods were found suitable :—

(*a*) Reduction with hydrogen in presence of platinum black which was prepared according to the method of Willstätter and Waldschimidt Leitz (*Koll.-chem. Beih.*, 1921, **54**, 113) and kept after purification under conductivity water.

(*b*) Reduction with hydrazine hydrate, always taking care that the dye to be reduced is in excess, so that the hydrazine hydrate added to the solution is completely decomposed. The gaseous decomposition products in this case were removed from the system by streaming with pure nitrogen.

Fig. 1 will make the procedure clear. 0.005% Dye solution was kept in the flask (1) which was gently heated and was reduced by streaming pure H_2 gas in presence of platinum black. The reduced product is very unstable and is easily oxidised by the oxygen of the air. Hence air is completely excluded from the system. The dye was reduced to the extent desired and was then transferred by excess of H_2 pressure to the flask

FIG. I.

Ultra-microscope Arrangement.

Pt. electrodes 9 and 10 leading to the H. T. cells, voltage
varying between 60 and 220.

7—Calomel decinormal electrode. The Pt. electrode 8 and
7 are joined to the potentiometer.

Pt. electrodes 3 and 4 are connected with the conduction
apparatus.

5—Cataphoretic cell.

6—Microscope.

containing colloidal gold after filtering the dye through a filter paper
attached to the tube (*b*). In order that the reduced dye might not be
oxidised by the oxygen of the air contained in the flask (2), H_2 gas
was first passed for five minutes in the gold sol, previous to admixture
with the dye solution. Then the reduced dye and the gold sol (1 : 1)
was mixed thoroughly by bubbling H_2 gas and allowed to attain the
temperature of the room.

This process of reducing dye was followed only in the case of gold
sol. We have observed that colloidal particles of platinum get coated
with a film of hydrogen gas which is not immediately removed by even
bubbling nitrogen. The particles showed irregular movement and the
velocity in the electrical field could not be measured. In this case the
dyes were partly reduced by hydrazine hydrate solution and through the
reduced dye N_2 gas was passed in order to avoid oxidation.

The colloidal solutions of gold and platinum were prepared by Bredig's
method in conductivity water.

The mixture of the reduced dye and the gold sol was allowed to
pass into the cataphoretic cell half an hour after stopping the current,

of H_2 or N_2. Then a high tension field was introduced through a variable resistance to the mixture (dye + sol) by the electrodes 9 and 10. By means of the commutator (C) the current was reversed. The cataphoretic movement was measured in both directions taking five observations in each direction by focussing at a depth of 0·14 diameter of the Mattson cell according to the equation

$$U\left(\frac{2a^2}{1^2} - 1\right) = 0 \quad \text{or} \quad a = \frac{r}{\sqrt{2}}$$

where a = distance from the axis or 0·14 of the cell's diameter in the case of Mattson cell.

The time required for a particle to pass through a definite distance of the micrometer scale in the microscope was observed by a stop-watch. The results were checked in typical cases by noting the cataphoretic speeds at different depths when a parabolic curve was obtained.

The particles of gold and platinum were as usual negatively charged.

Specific Conductivity of the Mixture (dye and sol) and the Potential Gradient in the System.—For this two platinum wires (3 and 4) were introduced into one of the side-tubes attached to the cataphoretic cell and the cell constant was determined by measuring the conductivity of a solution of KCl of known strength ($N/50$). The specific conductivity of the dye solutions containing the sol is then determined in each case and knowing the dimensions of the cataphoretic cell, it is possible to calculate the resistance of 1 c.c. of column of the dye solution in the observation cell. The current passing through the high tension circuit was read by the deflection of a calibrated galvanometer. The potential gradient in the cataphoretic cell was thus easily calculated.

E. M. F. Measurement.—The redox potential of the mixture was determined *in situ* by first switching off the high tension circuit and then measuring the potential of the platinum wire (8) against a known electrode $N/10$-KCl-calomel electrode (7) by a potentiometer.

p_H Measurement.—After the cataphoretic velocity had been determined mixture was taken out from the cataphoretic cell and the p_H of the mixture was measured by a glass electrode. The velocities were also measured at different depths of the cataphoretic cell and they were found to lie on a parabola. After every observation, the cell was cleansed by acid and alkali. The experimental data are recorded in the following tables.

J. C. GHOSH HND N. G. BASAK

TABLE I.

Gold Sol.

	Thionine.				Methylene blue.		
E_h.	Reduction.	p_H.	V_o.	E_h.	Reduction.	p_H.	V_o.
+0·0556	15%	8·0	$21\cdot4 \times 10^{-5}$	+0·015	7·0%	8·0	$25\cdot7 \times 10^{-5}$
+0·009	85·0	,,	25·7	−0·031	71·0	,,	27·8
−0·028	98·5	,,	28·9	−0·048	88·5	,,	31·5
+0·16	27·0	5·0	14·9	−0·063	96·0	,,	33·0
+0·09	99·0	,,	18·7	+0·18	1·0	5·0	13·9
+0·18	16·5	4·7	12·4	+0·136	7·0	,,	16·7
+0·103	11·0	6·8	16·8	+0·105	39·0	,,	17·6
−0·023	58·0	8·4	25·8	+0·32	99·5	,,	20·9
				+0·13	23·0	5·0	14·9
				+0·11	1·0	6·0	14·5

TABLE II.
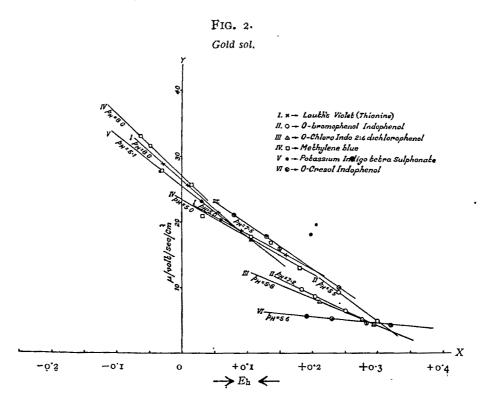
Platinum Sol.

	Thionine.				Methylene blue.		
E_h.	Reduction.	p_H.	V_o.	E_h.	Reduction.	p_H.	V_o.
+0·065	9·0%	8·0	$17\cdot3 \times 10^{-5}$	+0·0214	4·0%	8·0	$21\cdot0 \times 10^{-5}$
+0·0516	19·0	,,	18·3	−0·023	58·5	,,	23·1
+0·0105	78·0	,,	21·7	−0·052	92·0	,,	24·7
+0·18	30·0	4·5	10·1	+0·14	4·0	5·0	12·4
+0·13	96·8	,,	12·4	+0·101	52·0	,,	13·9
+0·10	94·0	5·0	15·2	+0·103	12·0	5·4	14·5
+0·12	42·0	5·3	12·0	+0·08	24·0	5·6	15·8
				−0·05	33·4	8·2	21·7

DISCUSSION.

Detailed investigations of the electrochemical properties of gold sol have already been carried out by Zsigmondy and co-workers, Pauli and co-workers, and by Beans and Eastlack and co-workers. It has been claimed by the last group of workers that gold sol by Bredig's method can only be prepared if the water contains traces of Cl ion. Pauli and Kautzki did not find any Cl ion, either in the gold gel or the filtrate from such a gel. Pauli maintains that the negative charge of gold sol is due to the surface being coated with $Au(OH)_4$ ion which is analogous in composition to $AuCl_4$ ion. In our experiments the colloidal particles of gold were treated with hydrogen gas before being admixed with a redox indicator dye, the reducing potential of both hydrogen and the dye being such as to reduce completely microscopic particles of gold oxide It is debatable whether in such an environment, the hydroxy gold ion is capable of stable existence.

The influence of OH^- ion on the cataphoretic speed of colloidal gold has been studied by Pauli and Fuels and Thiessen and Henmann. The values change from 30×10^{-5} approximately to 35×10^{-5}, when the final

FIG. 2.

Gold sol.

I. x — *Lauth's Violet (Thionine)*
II. o — *0-bromophenol Indophenol*
III. △ — *0-Chloro Indo 2:6 dichlorophenol*
IV. □ — *Methylene blue*
V. ● — *Potassium Indigo tetra Sulphonate*
VI. ● — *0-Cresol Indophenol*

concentration of K_2CO_3 added is $1 \times 10^{-3}N$. Our experimental results on the relation between the redox potential of the environment and the cataphoretic velocity of gold particles are shown in Fig. 2.

The observations relate to particles of ultramicroscopic sizes, and the redox potential has been varied by (i) choice of suitable indicators, (ii) by changes in the oxidant to reductant ratio, and (iii) by changing p_H by addition of ammonia and acetic acid.
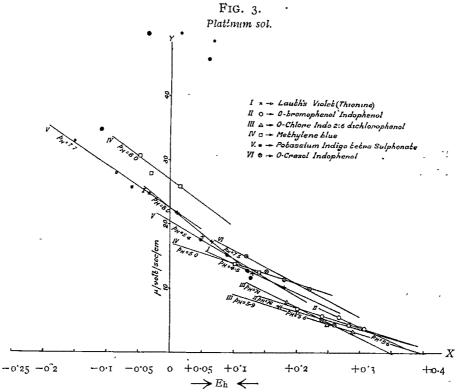
It will be seen that the slope of $E_h - \mu$ (cataphoretic speed) has approximately the same value for all the dye solutions studied. Not only that, the absolute values of μ in different dye solutions, and at different p_H are close to one another, if the redox potential is the same. It is to be noted that some of the dye ions are positively charged and others negatively charged, but their influence on the cataphoretic speed of the negatively charged gold particles is independent of the sign of the charge of the indicator ion, but is dependent on the redox potential of the environment.

The electrochemical properties of platinum sol have been thoroughly studied by Pennyquick (*J. Chem. Soc.*, 1927, 2600; 1928, 551) who postulates the existence of $H_2Pt(OH)_6$. We have observed that unlike the gold sol, hydrogen streamed through a platinum sol changes the surface of the sol particles in such a way that the cataphoretic speed could not be measured with reproducible exactitude. This created the suspicion that the molecules of hydrogen adsorbed by the sol particles adhere tenaciously to the surface and it takes a long time after the bubbling has been stopped before desorption becomes complete. This hypothesis could be tested if a clean platinum wire were dipped into a platinum sol, after it has been streamed with hydrogen, and the potential of the wire against a $N/10$-calomel electrode measured from time to time.

Time in minutes after stopping the hydrogen stream.	5	30	60	150	180
E_h of the platinum wire in platinum sol.	−0·09	−0·06	+0·34	+0·40	+0·45

It will be seen that the potential of the solution to begin with is negative and not far removed from the potential of the hydrogen electrode. After the 30th minute the adhering film of hydrogen practically disappears and the sol particles cannot function as a reservoir of hydrogen gas. This point is indicated by the sudden jump to high values of positive potential.

In view of this direct evidence of hydrogen film on the surface of colloidal platinum particle, it is worth considering, if the hexahydroxoplatinic acid is not completely reduced in contact with hydrogen.

FIG. 3.

Platinum sol.

I   x → *Lauth's Violet (Thionine)*
II o → *O-bromophenol Indophenol*
III △ → *O-Chlone Indo 2:6 dichlorophenol*
IV □ → *Methylene blue*
V. ● → *Potassium Indigo tetra Sulphonate*
VI ⊕ → *O-Cresol Indophenol*

The general features of E_h-μ curves in platinum sol (Fig. 3) are similar to those in gold sol.

It will be premature at this stage to try to draw far reaching conclusions from the results recorded here but the inference may easily be made that under the experimental conditions that we have maintained, the change in the cataphoretic speed and hence the electrokinetic potential of the gold and platinum particles are not probably due to any specific ion adsorption but are due to more general factors, the predominating one being the electron activity of the medium, which is responsible for the oxidation-reduction potential of the system. It is also to be noted that if the E_h-μ curves are extrapolated to zero value of μ, they all tend to cut the E_h axis between $+0.35$ and $+0.45$ volts. It is significant that these values of electrode potential are in the neighbourhood of these obtained by Billiter and Garrison.

Our thanks are due to Dr. S. K. Bhattacharya for his help in this investigation.

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11

REVIEW

The Chemical Constitution of Natural Fats.—By T. P. HILDITCH
(CHAPMAN & HALL LTD., LONDON) 1940. PP. XI + 438. PRICE 35 SH. NET.

Attempts have been made for the first time in this book to systematize natural oils and fats from biological and constitutional points of view. The author has classified them under the following heads :—

(1) Fats of aquatic origin
 (a) Fresh water
 (b) Marine

(2) Fats of land animals

(3) Milk fats

(4) Vegetable fats
 (a) Seed fats
 (b) Fruit pulp fats
 (c) Fruit carnel fats

and has shown the characteristic differences in their compositions specially in regard to component fatty acids and constituent glycerides. The old way of dividing oils and fats under non-drying, semi-drying and drying heads has been given up. This classification has served and will still serve some purpose ; it has reference to the presence of constituent oleic, linolic and linolenic acids in the three types of oils respectively but on account of their occasional simultaneous presence, one class always overlaps another and hence creates difficulty in thus distinguishing them. The classification will of course still be useful but the one adopted by the author seems to be more rational. Although the chemistry of various natural products such as carbohydrates, terpenes and alkaloids, has been quite well known due to enormous amount of research works on synthetic lines, that of natural oils and fats has been all along an obscure chapter. The characteristic values *e.g.*, Sap. value, Iodine value, Acetyl value, Reichert Meissel, Reichert Polenske and other values, the qualitative tests such as Maumene, R. I., Bromine Thermal, Elaidin etc., and the methods of isolation of component fatty acids *via* lead salts or by fractionation of esters—were all that helped us to gain an insight into the composition of oils and fats. At first isolation of glycerides was attempted by laborious fractional crystallisation with partial

or no success and then sporadic and sometimes fruitless attempts were made in synthesising glycerides. Due to the elastic nature of α-, β-, and γ-positions in the glyceryl radicle erroneous results were obtained in such syntheses as were shown by Emil Fischer who in his last days deveted his attention to this aspect and successfully prepared some of them by his novel method. In the case of natural products like carbohydrates, terpenes and alkaloids and colouring matters, preparation of substances in the pure state was first achieved ; then their analyses and reactions gave a comprehensive idea as regards their structures. These two were generally followed by their syntheses for final identification. These steps could not be adopted in the case of oils and fats on account of (a) the difficulty in getting individual glycerides in the pure state (natural oils and fats are mixtures generally of various kinds of glycerides), (b) the difficulty of determining the nature and respective positions of the component fatty acids and finally (c) the difficulty in synthesising the required glyceride for identification. While the first difficulty remains as ever, the second one has been partially tackled by Hilditch and his band of workers. The present book embodies all their results with the generalisations that have been revealed. Hilditch's works in this obscure line of organic chemistry started from 1925. His procedure, although not entirely novel as it followed the line of Bertram, developed in entirely new and interesting manner in its applications. It was a modification of Bertram's process of oxidation of glycerides ; this was followed by Haller's process of alcoholysis with a view to prepare different kinds of esters and fractionally separate them. Considering how light has been thrown in the constitutional meshes of complex glycerides we must say that the researches have no parallel. A mixture of complex glycerides (a), (b), (c), (d), etc., is oxidised in a controlled way so that part of the unsaturated residues is broken up at the double bond or bonds to give mono- or dicarboxy fatty acids on the one hand and mono,- di- or tri- acid glycerides on the other according as there are one, two or three unsaturated component fatty acids in the glyceride molecules ; the fatty acids are identified and the acid glycerides are esterified according to the Haller's method and fractionally separated. For example a glyceride of the composition :

$$
\begin{array}{l}
\text{C---R} \\
\quad | \\
\text{C---O·CO(CH}_2)m\text{·CH}=\text{CH·CH}_2\text{·CH}=\text{CH(CH}_2)n\text{·COOH} \\
\quad | \\
\text{C---R}^1
\end{array}
$$

(where R and R^1 are different saturated acid residues) when submitted to

Hilditch's process of oxidation would give malonic acid, $(CH_2)n\begin{cases} COOH \\ COOH \end{cases}$

and an acid glyceride of the composition

$$\begin{array}{l} C-R \\ | \\ C-O \cdot CO \ (CH_2)m \cdot COOH \\ | \\ C-R^1 \end{array}$$

After separation by esterification and fractional distillation, the product is completely hydrolysed and R, R¹ and m are found by further examination. It cannot be said that we have reached a perfect state as positions of R, R¹ and the third residue remain yet to be determined. The esterification method of separation (practically the only method) is also not beyond objection as pure stuff can not easily be obtained on the examination of which a strictly scientific conclusion may be based.

A fairly representative number of oils has been dealt with in the book with special reference to the constitutional aspects elaborated above. It has been written in an entirely novel manner unlike other text-books on oils; it will certainly be of help to research workers. General students will be naturally disappointed as many ordinary details have been omitted, many oils have not found place and technological aspects have been totally avoided. The author has in his preface sufficiently explained these omissions. The addition of the chapters on the constitution of the fatty acids—many of which remain still obscure, the synthetic glycerides and the special technique for the examination of oils by the new method has been quite valuable. The book may not be an ideal one for reference but it is undeniably the first to which the workers in the complicated field of oils will certainly look for guidance.

M. G.

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